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THE CHEMISTRY
OF THE
INORGANIC COMPLEX COMPOUNDS

An Introduction to
WERNER'S COORDINATION THEORY

BY

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Authorized Translation by

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AUTHOR'S PREFACE

THE purpose of this book is to present a synopsis of the Chemistry of the Inorganic Complex Compounds with as few details as possible. In most textbooks of Inorganic Chemistry in which the subject is considered, the treatment is too brief. In fact, the student who desires to study the theory more exhaustively fails to acquire a working knowledge of its principles, and, as a result, generally becomes discouraged at the prospect of studying Werner's "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," which, until a short time ago, was the only detailed work on complex compounds.

A reader who wishes to acquire a more complete knowledge will be obliged to consult Werner's classic treatise, the comprehension of which will be made easier by a preliminary study of this introductory book.

R. Weinland's "Einführung in die Chemie der Komplex-Verbindungen" (Enke), which appeared during the preparation of my monograph, has a similar purpose in view. I should like to refer to it those readers who desire a more extensive and detailed presentation of the subject.

ROBERT SCHWARZ.

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TRANSLATOR'S PREFACE

WERNER'S Coordination Theory has found such wide application in the different branches of Chemistry that an understanding of its principles is necessary for the chemist who keeps abreast of current chemical literature. So far as the writer is aware, there is only one monograph in English on this subject, viz., Hedley's translation (Longmans, 1911) of the Second Edition (1908) of Werner's "Neuere Anschauungen." Since the publication of this translation many fundamental contributions to the theory have been made which should be included in any study of the complex compounds. Also, the treatment in Hedley's work is more exhaustive than is necessary for the general reader.

The following pages contain a sufficient amount of material to give the beginner a conception of the fundamental principles of the Coordination Theory. With the permission of Professor Schwarz, a large number of references to the original literature has been added for the benefit of those who wish to study the subject more thoroughly. These references should enhance the value of the book to American and English readers. It is expected that this translation will stimulate sufficient interest in the theory to induce many chemists to consult the two more advanced monographs — Werner's "Neuere Anschauungen" (1920) and Weinland's "Komplex-Verbindungen" (1919).

The fact that no systematic terminology has been developed for the Coordination Theory in English has rendered necessary the adoption of certain terms for which there is no precedent. Any criticisms or suggestions in regard to these terms, or to any other part of the book, will be welcomed by the writer.

The translator wishes to acknowledge his great indebtedness to Professor Oskar Baudisch, Research Associate in Bio-

chemistry at Yale University, who was formerly a pupil of Alfred Werner. The work was undertaken at his suggestion, and he has contributed his wide knowledge of the subject during the preparation of the manuscript.

The few changes which were made in translating have been approved by Professor Schwarz.

The translator takes pleasure in acknowledging many valuable criticisms and suggestions by his former teachers at Yale University, Professors H. W. Foote, T. B. Johnson, and R. G. Van Name. The assistance of Dr. H. S. Hill and Dr. C. S. Palmer in correcting proofs should also be mentioned.

LAWRENCE W. BASS.

YALE UNIVERSITY,
New Haven, November, 1922.

ABBREVIATIONS

Am. Chem. J.	American Chemical Journal
Am. J. Sci.	American Journal of Science
Ann.	Justus Liebigs Annalen der Chemie
Ann. chim. phys.	Annales de chimie et de physique
Ann. Min.	Annales des Mines
Ann. Physik	Annalen der Physik
Atti accad. sci. Torino	Atti della reale accademia delle scienze di Torino
Ber.	Berichte der deutschen chemischen Gesellschaft
Biochem. Z.	Biochemische Zeitschrift
Bull. soc. chim.	Bulletin de la société chimique de France
Chem. News	Chemical News and Journal of Physical Science
Chem. Zentr.	Chemisches Zentralblatt
Chem. Ztg.	Chemiker Zeitung
Compt. rend.	Comptes rendus hebdomadaires des séances de l'académie des sciences
Gazz. chim. ital.	Gazzetta chimica italiana
J. Am. Chem. Soc.	Journal of the American Chemical Society
J. Chem. Soc.	Journal of the Chemical Society (London)
J. Phys. Chem.	Journal of Physical Chemistry
J. prakt. Chem.	Journal für praktische Chemie
Kong. Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar (Stockholm)
Monatsh.	Monatshefte für Chemie
Phil. Mag.	London, Edinburgh and Dublin Philosophical Magazine and Journal of Science
Pogg. Ann.	Poggendorffs Annalen der Physik und Chemie
Proc. Amer. Acad.	Proceedings of the American Academy of Arts and Sciences
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique
Z. anorg. Chem.	Zeitschrift für anorganische (und allgemeine) Chemie
Z. physik. Chem.	Zeitschrift für physikalische Chemie

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CHEMISTRY OF THE INORGANIC COMPLEX COMPOUNDS

CHAPTER I

INTRODUCTION

1. The Constitution of Chemical Compounds

a. Combining Weights

The chemical elements do not unite with one another in arbitrary and varying proportions by weight, but always in agreement with the Law of Definite Proportions. This experimental fact was discovered at the beginning of the nineteenth century and was later established conclusively by a large number of carefully performed quantitative analyses of chemical compounds. For all substances which have been investigated, it has always been found that in one and the same compound the proportion by weight of the elements is the same. It is known further that two elements may form several compounds with one another. Then, however, the weights of one of these elements which are combined with a fixed weight of the other element are in the ratio of simple whole numbers (Law of Multiple Proportions).

On the basis of these laws of definite and multiple proportions there is assigned to each element a fixed combining weight, which is identical with the percentage by weight determined analytically, referred to a number arbitrarily chosen as unity. From the values found by the analysis of water, 88.81 per cent oxygen and 11.19 per cent hydrogen, if oxygen is assumed equal

to 1.000 arbitrarily, the combining weight of hydrogen is 0.126. If the combining weight of the latter element is chosen as 1.000, the value for oxygen is then 7.94.

The ratio of the combining weights of the two elements is therefore approximately 1:8. The basis of the combining weights is taken as 8.000 for oxygen, so that no number less than 1.000 will be obtained, and the value for hydrogen, the element with the smallest relative weight, becomes 1.008. This number is, therefore, the (relative) combining weight of hydrogen.

If the percentage composition of any compound is subjected to similar calculations, the value of oxygen (equal to 8.000) being kept throughout as a standard, to each element may be assigned a certain number representing the amount by weight which always combines exactly with a similarly calculated weight of another element.

Hence, by means of quantitative analyses the combining weights of all the elements may be calculated on a common basis, and the following law may be formulated: The proportions by weight of all compounds are fixed by the combining weights or their rational multiples.

b. Atomic Weight and Valence

On the basis of phenomena which will not be described here, it is found that, in one molecule of water, one atom of oxygen is combined, not with one atom of hydrogen, but with two, and hence this substance is given the formula H_2O and not HO. Accordingly, the smallest proportion by weight of oxygen which is found in a molecule of a compound is not 8.000, but 16.000, or twice the combining weight. This smallest proportion by weight is called the (relative) atomic weight.

The atomic weight is equal either to the combining weight, as in the case of hydrogen, or to some integral multiple, double in the case of oxygen. Accordingly, oxygen has the power of holding two atoms of hydrogen, while some other elements may hold three or four.

If the valence or combining power of hydrogen as a standard is assumed to be one, it follows that other atoms may have different valences, depending upon whether they can unite with

one, two, or three hydrogen atoms, and these atoms are said to be univalent, bivalent, or trivalent, respectively. If no hydrogen compound of a given element is known, its valence may be deduced from a compound with some other univalent element, i.e., one which forms a compound with hydrogen containing one atom of each. The numbers obtained in this way are called valences.

From the formulæ:

HCl^{I}, H_2O^{II}, H_3As^{III}, H_4C^{IV},

Cl_5P^{V}, Cl_6W^{VI}, $O_7{}^{II}Mn_2{}^{VII}$, $O_4{}^{II}Os^{VIII}$,

we obtain the valences:

Cl 1, O 2, As 3, C 4,

P 5, W 6, Mn 7, Os 8.

If for any reason it is desirable to emphasize the valence, it may be indicated by a Roman numeral index as shown in the formulæ above.

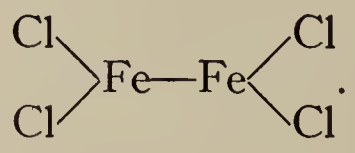
Valence may be defined as the number of atoms of hydrogen, or of any other univalent element, with which an atom of the element is combined, or which it replaces.

c. Variable Valence

The originator of the doctrine of valence, Kekulé,[1] brought forward the principle that the valence of each element has a constant, invariable value. This assertion was mainly based on the fact that the element carbon, throughout the enormous number of its compounds, is always quadrivalent. The existence of carbon monoxide, which might be assumed to represent an exception to the law, could be explained without great difficulty by the introduction of the conception of unsaturated valences. It was more difficult to bring into accord with the theory of constant valence the elements which clearly exert two different

[1] For an account of the early history of the valence theory see E. Hjelt's "Geschichte der organischen Chemie," Chapter XII; Vieweg (Braunschweig), 1916.

valences, and it was only by means of special formulæ for the disagreeing compounds that the valence relations of the elements could be made to agree with the favored valences. For example, ferrous chloride ($FeCl_2$) was given the formula Fe_2Cl_4 in order that iron need not show a valence of two in addition to the valence of three which it was supposed to exert. The graphic representation of the double molecular formula for ferrous chloride requires trivalent iron:



Besides the compound phosphorus trichloride (PCl_3), derived from trivalent phosphorus, phosphorus pentachloride (PCl_5) was also known. In this case the assertion was made, in behalf of the theory, that the pentachloride existed as a so-called addition compound of the formula $PCl_3 \cdot Cl_2$, and the evidence used in support of this assertion was the well-known decomposition or dissociation of the pentachloride in the gaseous state into the trichloride and chlorine.

More recent investigations, however, proved conclusively the impossibility of retaining the theory of constant valence. It was shown that phosphorus pentafluoride (PF_5), the analogue of the pentachloride, could be vaporized without dissociation;[1] that ferrous chloride should be given the simple formula $FeCl_2$ in accordance with the molecular weight in solution as determined by the cryoscopic method;[2] and, finally, that oxygen was able to form oxonium compounds,[3] and therefore could exist in the quadrivalent as well as in the bivalent condition.

It was therefore necessary to extend the theory of valence by assuming that some elements could exhibit more than one valence. An exception is made in the case of the element carbon,[4]

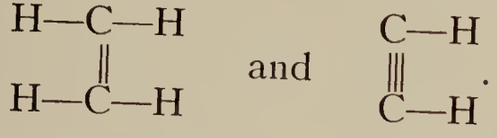
[1] T. E. Thorpe, Ann., **182**, 201 (1876).

[2] A. Werner, Z. anorg. Chem., **15**, 1 (1897).

[3] J. N. Collie and T. Tickle, J. Chem. Soc., **75**, 710 (1899); A. von Baeyer and V. Villiger, Ber., **34**, 2679, 3612 (1901); **35**, 1201 (1902); J. N. Collie, J. Chem. Soc., **85**, 971 (1904).

[4] A comprehensive discussion of the valence of carbon may be found in the translation by T. B. Johnson and D. A. Hahn of F. Henrich's "Theorien der organischen Chemie"; Wiley (New York), 1922.

which is generally considered quadrivalent, even in such compounds as C_2H_2 and C_2H_4, for convenience in discussing the reactions of its compounds. In the two substances mentioned, unsaturated valencies in the form of double or triple linkages are assumed, as indicated by the structural formulæ:



From a more careful examination of the compounds of a given element it becomes evident that the valence depends, first, upon the character of the other elements contained in the compound, and, second, upon external conditions, especially temperature.[1] For example, manganese can exert a valence of seven toward oxygen (Mn_2O_7), but a valence of only four toward chlorine ($MnCl_4$). Sulphur is bivalent in combination with hydrogen (H_2S), and sexivalent with oxygen and fluorine (SO_3, SF_6). At higher temperatures, however, sulphur no longer remains sexivalent in combination with oxygen, sulphur trioxide being unstable, but uses then only four valencies.

Accordingly it can be stated that the valence of an element is variable, but that in each special case it is fixed and can never be exceeded. When this value is reached the atom itself can no longer exert other bonds. The valence theory must hold firmly to this principle, because the theory would become objectless if exceptions were permitted in any individual case.

2. Inadequacies of the Valence Theory

Compounds of the Higher Order

The valence theory has been found to hold true for the explanation of the formation and behavior of all simple chemical compounds, but it does not suffice for compounds of the higher order. By the term " compound of the higher order " is meant any substance formed by the union of two or more saturated molecules, i.e., molecules in which all the valencies of the con-

[1] J. Billitzer, Monatsh., **25**, 745 (1904); R. Abegg and F. W. Hinrichsen, Z. anorg. Chem., **43**, 122 (1905).

stituents are satisfied. A general reaction to represent the formation of such a compound may be expressed by the equation:

$$AB + CD = AB \cdot CD.$$

Although, according to the valence theory, the saturated molecule AB has not the power of further addition, since the union of the atom A with the atom B has satisfied the valencies of both, addition nevertheless takes place between this saturated molecule and a similarly saturated molecule CD. An explanation of the forces which enable this process to take place can not be given by the valence theory. Yet these compounds of the higher order, which were formerly often called molecular compounds, play an important rôle in inorganic and organic[1] chemistry, as will be seen from a study of the subsequent pages. As representatives of the various classes we may cite:

$$\left.\begin{aligned} PtCl_4 + 2NH_3 &= PtCl_4 \cdot 2NH_3 \ ^{2} \\ CoCl_3 + 6NH_3 &= CoCl_3 \cdot 6NH_3 \ ^{3} \end{aligned}\right\} \text{Metal Ammine Salts}$$

$$\left.\begin{aligned} CaCl_2 + 6H_2O &= CaCl_2 \cdot 6H_2O \ ^{4} \\ SO_3 + H_2O &= H_2SO_4 \end{aligned}\right\} \text{Hydrates}$$

$$\left.\begin{aligned} KCl + AuCl_3 &= KAuCl_4 \ ^{5} \\ K_2SO_4 + Al_2(SO_4)_3 &= K_2Al_2(SO_4)_4 \ ^{6} \end{aligned}\right\} \text{Double Salts}$$

All these types, the metal ammine salts, the hydrates, and the double salts, are exactly alike in the manner of their formation. Their differences are apparent only in aqueous solution, in which they decompose into their components to varying degrees. Those compounds which exhibit considerable stability in solution

[1] P. Pfeiffer, "Organische Molekülverbindungen"; Enke (Stuttgart), 1922.

[2] C. Grimm, Ann., **99**, 80 (1856); P. T. Cleve, Kong. Vet. Akad. Handl., **10**, No. 93, pp. 41, 63 (1871); F. Hoffmann; Dissertation, Königsberg (1889), p. 18.

[3] S. M. Jörgensen, Z. anorg. Chem., **17**, 455 (1898); **19**, 78 (1899).

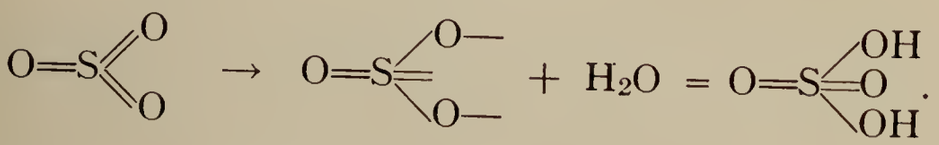
[4] H. W. B. Roozeboom, Z. physik. Chem., **4**, 31 (1889); Rec. trav. chim., **8**, 1 (1889).

[5] A. Lainer, Monatsh., **11**, 220 (1890); R. Fasbender, Chem. Zentr., **1894**, I, 409; II, 609.

[6] Gmelin-Kraut, "Handbuch der anorganischen Chemie," 7th Ed., Vol. II, Part 2, p. 659; Winter (Heidelberg), 1909.

and which lose the close attachment of their components only to a slight degree are called complex compounds. The methods by which the structure of the complex molecules and the extent of their decomposition have been determined will be discussed later. It must be emphasized particularly that there are innumerable intermediate stages between the completely stable, true complex salts and the completely decomposed, true double salts, and that, for this reason, a sharp distinction cannot be made.

It is worthy of note that the valence theory explains, apparently with success, that class of compounds of the higher order formed by the union of water with oxides of metals or non-metals, one of the most important classes of compounds in inorganic chemistry, by the assumption that the oxygen of the oxide possesses the power of adjusting its valencies. That is to say, the linkage of the oxygen changes from a double to a single bond, thus liberating momentarily a free bond for the molecule of water which is added:



This plausible explanation, however, does not satisfy all the conditions, as may be seen on closer inspection, since it can not be applied to the completely analogous addition of molecules to the compounds of univalent non-metals. In the latter case no valency can be set free by adjustment of the atoms and, therefore, some other mechanism must be suggested. Any proposed scheme must be applicable both to molecular compounds containing oxygen, as, for example,

$$K_2O + SO_3 = K_2SO_4,$$

and to compounds containing univalent elements, as in

$$KCl + AuCl_3 = KAuCl_4.$$

There is still another objection to the explanation given by the valence theory. If all oxides were actually able to add water by adjustment of the oxygen atoms, then, consequently, the

following hydroxyl compounds of the elements of the second period of the Periodic System (Si, P, S, Cl) would result:

$$Si(OH)_4, \quad P(OH)_5, \quad S(OH)_6, \quad Cl(OH)_7.$$

In place of these compounds the following actually exist:

$$Si(OH)_4, \quad PO_4H_3, \quad SO_4H_2, \quad ClO_4H.$$

It follows, therefore, that each of these elements, without regard to the composition of the anhydrous oxide, is able to hold in combination only four oxygen atoms and exactly the same number of hydrogen atoms that is bound directly to it in its hydride:

$$SiH_4, \quad PH_3, \quad SH_2, \quad ClH.$$

These harmonizing phenomena indicate that the explanation of the formation of such addition compounds with water is not to be sought in the production of hydroxyl groups by adjustment of the oxygen atoms, but in the power of each element to hold in union four oxygen atoms to satisfy all of its valencies. In agreement with this conclusion, it is found that the oxides of osmium and ruthenium, OsO_4 and RuO_4, are entirely unable to form acids by the addition of water.

Accordingly, the explanation of the origin of compounds of the higher order given by the valence theory appears forced in the single case to which it is applied and is wholly inapplicable to all other cases. It is, therefore, necessary to abandon the theory, or at least to enlarge upon it, in order to comply with the facts. This extension of the theory is accomplished by means of the so-called Coordination Theory.

CHAPTER II

THE COORDINATION THEORY

1. The Theory of Auxiliary Valences

In order to explain the fact that a molecule which, according to the valence theory, is saturated and complete still contains sufficient combining power to link other molecules firmly to itself, A. Werner introduced the conception of auxiliary valence; he states this new principle in the following words:[1]

"Even when, to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valencies, may be called into action."

We shall consider, in order to visualize the conceptions and value of this theory, some of the compounds of the higher order mentioned previously, and first, the compound $PtCl_4 \cdot 2NH_3$.

If an aqueous solution of this compound is studied, the astonishing fact is observed that it gives no precipitate of silver chloride when treated with silver nitrate.[2] From this fact it must be concluded that the chlorine atoms are not transformed into ions by dissociation. If the conductivity of the solution is measured, it is observed that the value is extremely low,[3] and, consequently, the degree of dissociation must be nearly zero.

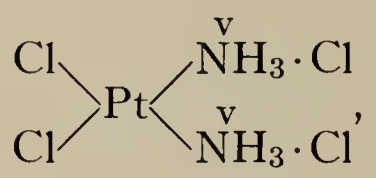
[1] A. Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 4th Ed., p. 44; Vieweg (Braunschweig), 1920.

[2] C. Gerhardt, Ann., **76**, 307 (1850).

[3] A. Werner and C. Herty, Z. physik. Chem., **38**, 351 (1901).

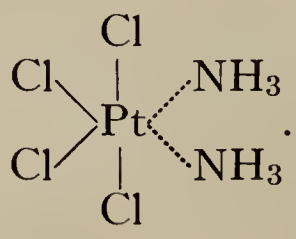
What formula may now be assigned to such a compound on the basis of its behavior in solution?

According to the valence theory, which places the valence of platinum at four, we might suggest the formula:[1]



which represents, so to speak, a type of substitution product of ammonium chloride. In this formula the nitrogen atoms, which have become quinquivalent, take upon themselves the task of binding the chlorine and platinum atoms. Hence the formula is incorrect, because such a compound, in analogy with ammonium chloride, should have a high conductivity in aqueous solution. Also, silver nitrate should precipitate at least two chlorine atoms from it. Both of these properties are lacking, as has previously been stated.

However, with the aid of the auxiliary valence theory a formula may be proposed which is in accord with all the observed phenomena:

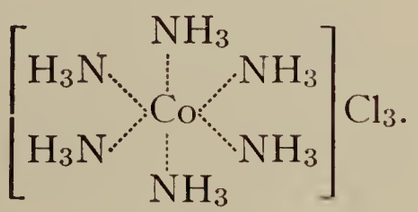


Besides its four principal valencies, the platinum atom also exerts two auxiliary valencies, which are used in holding the two ammonia molecules. These auxiliary valencies, indicated in the formula by broken lines, act in such a manner that the ammonia molecules enter into direct union with the platinum atom without causing any change at all in the direct union of the chlorine atoms. It is to be emphasized that more than two ammonia molecules can not be added without producing a profound change in the behavior of the chlorine atoms. Moreover, it should be noted that the total number of added atoms and molecules is equal to six.

[1] Cf., C. W. Blomstrand, "Chemie der Jetztzeit," p. 280; Heidelberg, 1869.

A second metal ammine compound, $CoCl_3 \cdot 6NH_3$, will now be considered. This salt is a good conductor of electricity in aqueous solution.[1] It is an electrolyte, the anion of which may be identified as the chlorine ion by the precipitate formed with silver ion. From a quantitative analysis it is found, besides, that all three chlorine atoms of the compound are precipitated by silver nitrate. If the solution is treated with sulphuric acid, the corresponding sulphate is produced,[2] but, strangely enough, the ammonia molecules are not removed by the treatment with strong acid.

From this behavior the compound is given the following formula on the basis of the auxiliary valence theory:



We assume that the addition of the six molecules of ammonia takes place by means of auxiliary valencies. They stand in direct union with the cobalt atom, which functions as the "central atom" of the complex. In this complex union, not only the specific characteristics of the ammonia, but also those of the cobalt, are lost. On the other hand, the chlorine atoms still retain their typical properties; e.g., they are precipitated by silver nitrate and therefore exist as ions in solution, a fact which is confirmed by the conductivity of a solution of the compound. A different, indirect union is assumed for them; they stand outside the true "nucleus," which forms, as such, a closed unit indicated in the structural formula by brackets. In this compound there are again six single units linked in the complex nucleus.

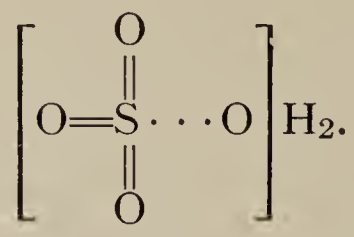
The structure of the previously mentioned oxygen compounds, to which the valence theory gives a separate place, may be explained satisfactorily from the same point of view. The formation of sulphuric acid from sulphur trioxide and water

[1] A. Werner and A. Miolati, Z. physik. Chem., **14**, 506 (1894).
[2] S. M. Jörgensen, Z. anorg. Chem., **17**, 457 (1898).

results from the fact that the sulphur atom, according to the equation

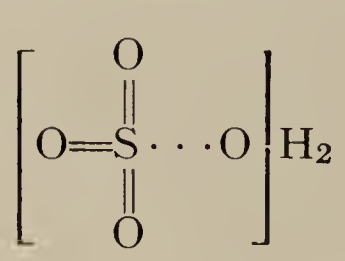
$$O_3S+OH_2=O_3S\cdots OH_2,$$

links with the oxygen atom of the water by the action of one auxiliary valency, and thus becomes the central atom of a complex nucleus:

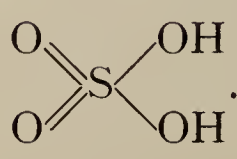


The hydrogen atoms are in loose, indirect union and are dissociated as ions in aqueous solution.

In cases where double bonds are present there is naturally no objection to the assumption that a secondary rearrangement may take place, resulting in a structure which is familiar from the valence theory. For example, the complex compound



may rearrange to



However, this is not at all probable, since the completely analogous addition compounds, such as $PtCl_4\cdot(NH_3)_2$, in which rearrangement is impossible, are very stable.

2. General Constitution of the Complex Compounds

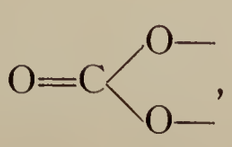
From the examples which have been considered, we learn that the platinum atom, as well as the cobalt atom, in its position as central atom, is in a condition to link to itself a total of six radicals or molecules, with the formation of a complex nucleus,

while the sulphur atom, on the other hand, is linked to four groups.

These " coordinated " groups are located in the first or inner sphere. The integer which indicates the number of such groups is called the coordination number. The maximum coordination number [1] shows how many groups at most can be held in the inner sphere of an element. For platinum it is six, for sulphur, four. The majority of the metals have the coordination number six, while the non-metals phosphorus, carbon,[2] nitrogen, and boron, as well as sulphur, have the number four.

Outside the nucleus are located the atoms which are attached by chemical valence to the whole molecule, and because of this position they exhibit a weaker union or an indirect linkage. A result of this loose linkage is the ease with which such atoms are split off as ions in aqueous solution. They may therefore be said to be in ionizable linkages.

It is characteristic of a coordination number that it is independent of the nature of the radicals or molecules attached to the central atom.[3] It has the same value whether neutral water molecules, acid radicals such as Cl', Br', NO_2', CN', hydroxyl groups, oxygen atoms, or ammonia molecules are present. Each of these, regardless of whether it has a valence of zero, one, or two, occupies only one coordination position. Multivalent acid radicals, however, such as SO_4'', CO_3'', C_2O_4'', can occupy either one or two positions.[4] To explain this apparent exercise of choice, we may say that such radicals have free valencies on different spacially separated atoms, in the case of the carbonate radical [5] indicated by



and may, therefore, occupy two coordination positions also. That a question of this kind of spacial arrangement actually

[1] A. Werner, "Neuere Anschauungen," pp. 51–55.
[2] See, however, A. Hantzsch, Ber., **54**B, 2627 (1921).
[3] A. Werner, loc. cit., p. 52.
[4] A. Werner, loc. cit., pp. 55–57.
[5] A. Werner and N. Goslings, Ber., **36**, 2378 (1903).

plays an important part will be evident from the stereochemical considerations which will be discussed later.[1]

A general survey of the multitude of complex compounds confirms the important decision that the different elements do not all possess the same ability or inclination to form complex compounds.

Few compounds have been studied in which an alkali metal forms the central atom of a complex nucleus. On the other hand, the majority of the compounds of the noble metals are of a complex nature. From a consideration of the electromotive series, in which the electrical potentials of the metals are indicated, we find that, in general, the tendency to form complex compounds increases with decreasing electrical potential. This fact may be explained by the assumption that ions of metals of low potential, the " weak " ions, deprive themselves of their independent ion formation by addition to other ions or to neutral substances. In a complex ion the atom which has little affinity for electricity is not forced to carry its charge alone, but shares the burden, so to speak, with other atoms.

As examples of complex compounds with alkali metal central atoms, we may cite [2]

$$[K(S{:}C(NH_2)_2)_4]I \quad \text{and} \quad [Cs(S{:}\,C(NH_2)_2)_6]Cl.$$

In the compound carnallite,[3]

$$KCl \cdot MgCl_2 = [MgCl_3]K,$$

the magnesium atom acts as the central atom of the nucleus $[MgCl_3]$. In this example, to be sure, because of the still important electrical potential, such a strong dissociation into the individual components takes place in aqueous solution that the compound must be regarded rather as a typical double salt than as a complex compound.

[1] See p. 57.

[2] A. Rosenheim and W. Löwenstamm, Z. anorg. Chem., **34**, 75 (1903); See also, O. Baudisch, Biochem. Z., **106**, 134 (1920).

[3] Gmelin-Kraut, Vol. II, Part 2, p. 481.

The ability to form stable complex salts first appears in zinc, iron, cobalt, and nickel, a few well-known examples of such salts being given in the following list:

$[Zn(NH_3)_4]Cl_2$,[1] $[Fe(CN)_6]K_4$,[2] $[Co(NO_2)_6]K_3$,[3] $[Ni(CN)_4]K_2$.[4]

At the bottom of the electromotive series, in the noble metals silver, platinum, and gold, the tendency to form complex compounds finally reaches its maximum. As examples we may mention the compounds

$[Ag(NH_3)_2]Cl$,[5] $[PtCl_6]H_2$,[6] $[AuCl_4]H$.[7]

In an entirely analogous manner non-metals and radicals, which exist as anions in solution, show more or less tendency to form complexes, depending upon the magnitude of their electrical potentials. The very weak acids [8] either show a strong tendency to enter the nucleus as coordinated radicals, or form complex compounds by themselves. As particularly applicable examples, we may mention here the many complex cyanides which result from the union of the weak cyanide ion with almost all the metals low in the electromotive series, and which are distinguished by their great stability. Characteristic examples of the type in which the weak acid radicals themselves act as central groups in a complex acid are silicotungstic, borotungstic, phosphotungstic, and phosphomolybdic acids. In these compounds WO_3 or

[1] A. A. Blanchard, J. Am. Chem. Soc., **26**, 1326 (1904).

[2] F. H. Getman, J. Phys. Chem., **25**, 147 (1921); O. Baudisch and L. W. Bass, Ber., **55B**, 2698 (1922).

[3] N. W. Fischer, Pogg. Ann., **74**, 124 (1848); E. Saint-Evre, Compt. rend., **33**, 166 (1851); **35**, 552 (1852); A. Rosenheim and I. Koppel, Z. anorg. Chem., **17**, 42 (1898).

[4] Gmelin-Kraut, Vol. V, Part 1, p. 135.

[5] Terreil, Compt. rend., **98**, 1279 (1884); Bull. soc. chim. [2] **41**, 597 (1884).

[6] J. Thomsen, J. prakt. Chem. [2] **15**, 297 (1877); L. Pigeon, Compt. rend., **120**, 681 (1895).

[7] R. Weber, Pogg. Ann., **131**, 445 (1867); F. Lengfeld, Am. Chem. J., **26**, 328 (1901).

[8] An indication of the weakness of an acid is the degree of hydrolysis of its salts in aqueous solution. Salts with weak anions, which unite with the hydrogen ions of water to form undissociated molecules, react alkaline because of the hydroxyl ions set free.

MoO_3 adds to the acids, just as the ammonia does in the metal ammines, according to the following equations:[1]

$$H_4SiO_4 + 12WO_3 + 2H_2O = [Si(W_2O_7)_6]H_8,$$
$$H_3BO_3 + 12WO_3 + 3H_2O = [B(W_2O_7)_6]H_9,$$
$$H_3PO_4 + 12WO_3 + 2H_2O = [P(W_2O_7)_6]H_7,$$
$$H_3PO_4 + 12MoO_3 + 2H_2O = [P(Mo_2O_7)_6]H_7.$$

3. Complex Anions and Cations

We shall now consider from the standpoint of the Coordination Theory some compounds of the higher order, particularly the well-known salt, potassium chloroplatinate,[2] which is so familiar from its applications in analytical chemistry. Since it results from the union of 2KCl with $PtCl_4$, it is indubitably a molecular compound.

From the conductivity of the salt in aqueous solution [3] it is found that it dissociates into three ions,[4] among which potassium ion may be detected analytically, but no chlorine ion. If the solution is treated with silver nitrate the precipitate is not silver chloride, but instead, a salt of the composition Ag_2PtCl_6.[5]

We must conclude, therefore, that the ion $PtCl_6''$ is present in the solution. On the basis of the Coordination Theory we infer that the platinum atom, which was originally combined by principal valencies with four chlorine atoms, has added two more by auxiliary valencies, thus forming the complex

$$[PtCl_6].$$

[1] A. Miolati, J. prakt. Chem., [2] **77**, 439 (1908); A. Rosenheim and F. Kohn, Z. anorg. Chem., **69**, 247 (1911); A. Rosenheim and M. Weinheber, ibid., **69**, 261 (1911); P. Pfeiffer, ibid., **105**, 26 (1919).

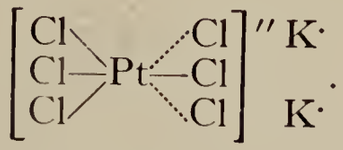
[2] K. Seubert, Ann., **207**, 11 (1881); W. Halberstadt, Ber., **17**, 2965 (1884); W. A. Noyes and H. C. P. Weber, J. Am. Chem. Soc., **30**, 15 (1908); E. H. Archibald, Z. anorg. Chem., **66**, 169 (1910).

[3] A. Werner and A. Miolati, Z. physik. Chem., **14**, 507 (1894).

[4] The molecular conductivity of electrolytes which give the same number of ions is of the same order of magnitude (see p. 22). K_2PtCl_6 has approximately the same conductivity (256) as $CaCl_2$ or $MgCl_2$ (234 or 223), both of which give three ions per molecule.

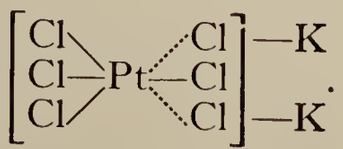
[5] L. Pigeon, Ann. chim. phys., [7] **2**, 482, 485 (1894).

This complex, however, is not electrically neutral, as was the compound $PtCl_4(NH_3)_2$ mentioned previously, since it acts as a conductor. It is therefore in solution as an ion, and, moreover, as an anion, a fact which is evident from its behavior toward silver ion. For these reasons the constitutional formula of K_2PtCl_6 must be given as



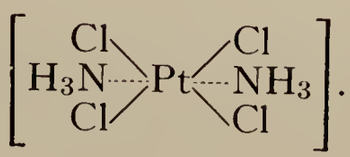
The question now arises as to when a complex is electrically neutral, positive, or negative. Why is $[PtCl_4(NH_3)_2]$ neutral and $[PtCl_6]''$ electronegative?

From the formula above we see that four of the chlorine atoms are thought to be attached by principal valencies and two by auxiliary valencies; the correctness of this assumption will be discussed below. In the latter two atoms the principal valencies are unsaturated and the two potassium atoms may attach themselves at these points:



The potassium ions leave behind, on dissociation in solution, the complex $[PtCl_6]''$ with two negative charges.

In $[PtCl_4(NH_3)_2]$, on the other hand, two saturated ammonia molecules are bound by auxiliary valencies to the platinum atom, the principal valencies of which are also satisfied. In the compound there are no valencies unsatisfied and therefore the molecule is electrically neutral:



The formulation employed above is very useful for a comprehension of the valence of a complex nucleus, but we cannot state that it is actually correct, since in the formulation of potassium chloroplatinate two chlorine atoms are linked in a different

manner from the other four. There is, however, no difference in the properties of the six, since they can be displaced by hydroxyl groups in the same manner, with the formation of the compounds from $[PtCl_5(OH)]H_2$ up to $[Pt(OH)_6]H_2$.[1] It follows, therefore, that the method of linkage is identical, since the action of the valencies is shown to be the same.

No real difference between principal valencies and auxiliary valencies is found to exist in complex nuclei. Rather, the central atom possesses an equally divided sum of forces which finds numerical expression in its coordination number.[2] In the following pages, therefore, no difference will be indicated in structural formulæ between principal and auxiliary valencies.

While, in the compound K_2PtCl_6, the complex functions as a negative ion, there are, conversely, positive complex ions also. We see all the important possibilities most clearly in the following table of the various cobalt complexes. The regularities which are observed in this series hold good for all complex compounds.

	Formula	The Complex is a	$V-R=W$ [3]
I.	$[\overset{III}{Co}(NH_3)_6]Cl_3$ [4]	trivalent cation	$3-0=+3$
II.	$[Co(NH_3)_5Cl]Cl_2$ [5]	bivalent cation	$3-1=+2$
III.	$[Co(NH_3)_4Cl_2]Cl$ [6]	univalent cation	$3-2=+1$
IV.	$[Co(NH_3)_3(NO_2)_3]$ [7]	neutral	$3-3=0$
V.	$[Co(NH_3)_2(NO_2)_4]K$ [8]	univalent anion	$3-4=-1$

[1] Cf., I. Bellucci and N. Parravano, Z. anorg. Chem., **45**, 142 (1905).

[2] Cf., P. Pfeiffer, Z. anorg. Chem., **112**, 81 (1920); W. Kossel, Ann. Phys., [4] **49**, 229 (1916).

[3] V = valence of central atom, R = number of univalent acid radicals, and W = valence of complex nucleus. See p. 20.

[4] S. M. Jörgensen, Z. anorg. Chem., **17**, 455 (1898); **19**, 78 (1899).

[5] E. J. Mills, Phil. Mag., [4] **35**, 251 (1868); C. D. Braun, Ann., **142**, 54 (1867); S. P. L. Sörensen, Z. anorg. Chem., **5**, 369 (1894).

[6] F. Rose, " Untersuchungen über ammoniakalische Kobaltverbindungen," p. 44, Heidelberg, 1871; G. Vortmann, Ber., **10**, 1454 (1877); A. Werner and A. Klein, Z. anorg. Chem., **14**, 33 (1897).

[7] S. M. Jörgensen, Z. anorg. Chem., **5**, 192 (1894); **13**, 175 (1897).

[8] S. M. Jörgensen, J. prakt. Chem., [2] **23**, 249 (1881) (Note).

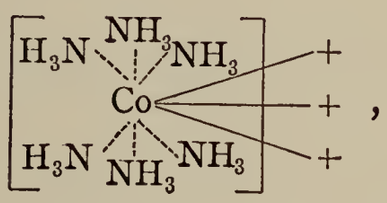
VI. $[\underset{\text{unknown}}{Co}(NH_3)(NO_2)_5]K_2$

$[\overset{III}{Fe}(NH_3)(CN)_5]Na_2$ [1] bivalent anion $3-5=-2$

VII. $[Co(NO_2)_6]K_3$ [2] trivalent anion $3-6=-3$

4. The Valence of Complex Nuclei

When the cobalt atom adds six molecules of ammonia, a complex nucleus is obtained in which, according to the preliminary formula previously given, all three valencies of the cobalt nucleus remain free,

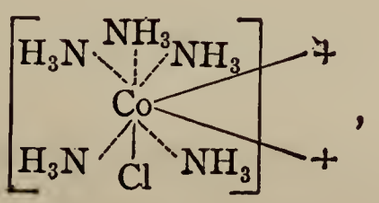


because the ammonia molecules require only auxiliary valencies. There is formed a trivalent cation or the corresponding triacid base

$$[Co(NH_3)_6](OH)_3,$$ [3]

which forms the salt (I) when it reacts with three molecules of hydrochloric acid.[4]

If the complex nucleus contains only five neutral molecules and one chlorine atom, a diacid base results which, according to the formula



[1] K. A. Hofmann, Ann., **312**, 1 (1900).

[2] N. W. Fischer, Pogg. Ann., **74**, 124 (1848); E. Saint-Evre., Compt. rend., **33**, 166 (1851); **35**, 552 (1852); A. Rosenheim and I. Koppel, Z. anorg. Chem., **17**, 42 (1898).

[3] E. Fremy, Compt. rend., **32**, 509, 808 (1851); Ann. chim. phys., [3] **35**, 257 (1852).

[4] E. Fremy, J. prakt. Chem., **57**, 95 (1852).

contains two unsaturated principal valencies. This base forms salts of type II.

If two univalent acid radicals enter the complex, two valencies of the central atom are held, or one valency remains free for the radical in the second or outer sphere, and the base is monacid (Salt III).

Compound IV is neutral, neither acid nor base, since all the principal valencies are retained in the nucleus by the three nitrite radicals. The compound does not conduct the electric current in aqueous solution,[1] nor does it split off any ions, and hence it does not give the test for the nitrite ion.

All that was said above in the consideration of K_2PtCl_6 holds also for salts V, VI, and VII. The metal atom, usually known only as a cation, becomes the central atom of a negative complex nucleus or anion, while the excess of negative acid radicals, which can not be held by principal valencies of the cobalt, comes into activity in the inner sphere. In the well-known potassium cobaltinitrite (VII), six nitrite radicals, in agreement with the coordination number, are held around the cobalt atom, the six valencies of the radicals being partly saturated by the three of the central atom and partly by three molecules of any base reacting to form a salt:

$$[\overset{III}{Co}(NO_2)_6]H_3+3KOH=3H_2O+[Co(NO_2)_6]K_3.$$

If we wish to obtain a general rule from this example, we may formulate it as follows:

$$W=V-R,$$

in which W stands for the valence of the complex nucleus, V for the valence of the central atom, which is familiar from the ordinary valence theory, and R for the number of chemically univalent radicals.

If V is greater than R, the value of W is positive, from which fact it may be seen that the complex is positively charged; i.e.,

[1] A. Werner and A. Miolati, Z. physik. Chem., **12**, 48 (1893); **21**, 227 (1896).

it is a cation. If V is equal to R, then W is equal to zero, and the complex is electrically neutral and has a valence of zero. If V is less than R the complex is negatively charged and is an anion.

Example: $[\overset{III}{Co}(NH_3)_4Cl_2]$; $V=3$, $R=2$,

$$W=3-2=+1.$$

The nucleus carries one positive charge and is a univalent cation.

Example: $[\overset{IV}{Pt}Cl_6]$; $V=4$, $R=6$,

$$W=4-6=-2.$$

The nucleus carries two negative charges and is therefore a bivalent anion.

It must be emphasized at this point that bivalent acid radicals, such as $[SO_4]''$, also require two valencies of the central atom in the nucleus, and that hence the number R, representing the total valences of these radicals, must be corrected accordingly. For example, the complex shown below is univalent:

$$[\overset{III}{Co}(NH_3)_5(\overset{II}{S}O_4)]; \quad W=3-2=+1.$$

5. The Electrolytic Dissociation of Complex Salts

Our knowledge as to whether a complex nucleus has acidic, basic, or neutral character is based primarily upon its behavior in aqueous solution. By electrolytic dissociation in solution it is possible for a complex to show itself either as an anion or as a cation.

In explaining the structure of a complex compound this dissociation is of the greatest importance, since it is possible to determine from it the number of individual ions produced.

In the case of chloro-pentammine-cobalti chloride,[1]

$$Co(NH_3)_5Cl_3,$$

[1] In regard to this nomenclature see pp. 24–26.

for example, the formation of three different complex nuclei is possible:

$$[Co(NH_3)_5Cl_2]Cl \qquad (I)$$

$$[Co(NH_3)_5Cl]Cl_2 \qquad (II)$$

$$[Co(NH_3)_5]Cl_3. \qquad (III)$$

Salt I is a binary electrolyte, since it dissociates into two ions, II is ternary, and III is quaternary. If formula II is recognized by analysis as the correct one, because of the fact that one of the chlorine atoms does not respond to the specific chlorine ion reaction, a still more clinching proof is the definite determination that we are dealing with a ternary electrolyte.

The molecular conductivities of all salts dissociating into the same number of ions are quite close together in numerical value and are unmistakably different from those of other salts giving a different number of ions. At 1000 l. dilution and 25° C., for binary electrolytes (NaCl, KCl) the value is about 125, for ternary ($BaCl_2$, $CaCl_2$, $MgBr_2$) about 250, and for quaternary ($AlCl_3$, $FeCl_3$) about 425.

The molecular conductivity of the chloro-pentammine-cobalti chloride in question is found by experiment to be 244.[1] This value approximates that given above for ternary electrolytes, from which fact it follows that the compound $Co(NH_3)_5Cl_3$, in accordance with Formula II, dissociates into three ions:

$$[Co(NH_3)_5Cl]Cl_2 \rightleftarrows [Co(NH_3)_5Cl]^{\cdot\cdot} + 2Cl'.$$

In a similar manner, by measurement of the conductivities of many complex compounds, the correctness of the formulæ assigned to them has been proved. At the same time, the agreement found has afforded an additional confirmation of the Coordination Theory.

If the chemical properties of a complex nucleus existing as an ion in solution are examined, it is found that ionic reactions applicable only to the central atom or to the coordinated radicals have disappeared and are replaced by new ones. A great deal has already been said about the failure of the chlorine ion reaction

[1] A. Werner and A. Miolati, Z. physik. Chem., **14**, 511 (1894).

with silver nitrate in the case of chlorine atoms held in a complex nucleus, and this phenomenon is often one of the most powerful aids in deciding questions of structure.

The characteristic reactions of the components have not, however, completely disappeared. Even if a new characteristic reaction is found for each complex ion, a more careful examination often reveals an especially sensitive reaction of a component. This means, of course, that some dissociation of the complex nucleus into ions, small though it may be, must have taken place.

As has already been emphasized in the introduction,[1] there is consequently no distinction between double salts, which are completely dissociated in aqueous solution, and complex salts. On the contrary, the difference is merely one of degree.

In the case of $H_2[PtCl_6]$, characteristic $[PtCl_6]''$ reactions are of course known, such as the precipitation with $K^{\cdot}$ or $NH_4^{\cdot}$ ions,[2] thus showing the ionization

$$H_2PtCl_6 \rightleftarrows 2H^{\cdot} + [PtCl_6]''.$$

Since, however, the S''-ions of hydrogen sulphide give a precipitate of PtS_2, [3] it follows that there is also a secondary ionization,

$$[PtCl_6]'' \rightleftarrows Pt^{\cdot\cdot\cdot\cdot} + 6Cl',$$

which is so extensive that the solubility product constant of PtS_2 is exceeded. Complex ions which possess sufficient power to hold their constituents together and to prevent further ionization are designated as strong complexes; those which have not this power are said to be weak.

Since the reactions of the constituents disappear, to a greater or less extent, specific complex ion reactions are generally used in analytical chemistry. The iron in the complex $[Fe(CN)_6]'''$, for which the iron ion test fails, is detected by the reaction

[1] Page 7.

[2] G. Kirchhoff and R. Bunsen, Pogg. Ann., **113**, 372 (1861); W. Crookes, Chem. News, **9**, 37 (1864); E. H. Archibald, W. G. Wilcox, and B. G. Buckley, J. Am. Chem. Soc., **30**, 752 (1908).

[3] U. Antony and A. Lucchesi, Gazz. chim. ital., **26**, I, 213, 215 (1896).

which the ferricyanide ion undergoes with ferrous ion with the formation of $[\overset{III}{Fe}(CN)_6]_2\overset{II}{Fe}_3$ (Turnbull's blue).

On the other hand, transformation into certain complex salts may be used for the separation of two elements,[1] as in the case of copper and cadmium;[2] hydrogen sulphide precipitates cadmium as sulphide from $[Cd(CN)_4]''$, while the analogous $[Cu(CN)_3]''$ is stable.

Finally, in this connection it must be remembered that in electrolytic analysis, as well as in electroplating, soluble complex compounds are often used because the precipitates produced from their solutions are particularly even and tenacious. For example, gold is precipitated from a solution of the chloride only as a brown powder, while from a solution of the complex salt $[Au(CN)_4]K$ it separates as a tenacious and lustrous coating.[3]

It must be noticed here that the anion $[Au(CN)_4]'$ does indeed migrate to the anode, but, as a result of the slight dissociation of the complex according to

$$[Au(CN)_4]' \rightleftarrows Au''' + 4CN',$$

a small quantity of gold ion is present which separates out at the cathode. By this means the equilibrium is destroyed, more complex ions decomposing with the formation of gold ions which again migrate to the cathode, until finally all the gold has been deposited on that pole.

6. Nomenclature

The majority of complex compounds have so complicated a constitution that any nomenclature based upon the usual system of designation would be ambiguous if applied to them. It was therefore necessary to create a logical, uniform nomenclature. The principles of the system which is used are briefly reviewed in the following paragraphs.

[1] A. C. Chapman, J. Chem. Soc. **111**, 203 (1917). This paper contains a summary of analytical methods involving the use of complex salts.

[2] J. Stieglitz, "The Elements of Qualitative Analysis," Vol. I, pp. 228–9; Century (New York) 1916.

[3] Cf., H. E. Medway, Am. J. Sci., [4] **18**, 56 (1904); F. F. Exner, J. Am. Chem. Soc., **25**, 896 (1903).

All nuclei or complexes are described in such a manner that the names of the coordinated groups precede the name of the central atom. The following sequence is observed: first, the acid radicals

Cl' (chloro), CO_3'' (carbonato), SCN' (thiocyanato);

then such groups as

H_2O (aquo), O (oxo), O_2 (peroxo), OH (hydroxo),

ethylene diamine (en), pyridine (Py), or other molecules related to ammonia, and, finally, immediately before the name of the central atom, ammonia, which is designated as the ammine group.[1]

Following the name of the complex are the acid radicals not present in the nucleus or inner sphere.

If the complex is an anion, the termination *-ate*[1] is added to the name.

The valence of the central atom is shown by the ending, which is the same as that of the type compound of the first order. To avoid any further cases of ambiguity, the following designations are used:[2, 3]

univalent atoms have the ending	a
bivalent atoms have the ending	o
trivalent atoms have the ending	i
quadrivalent atoms have the ending	é[4]
quinquivalent atoms have the ending	an
sexivalent atoms have the ending	on
septivalent atoms have the ending	in
octovalent atoms have the ending	en

[1] Three changes have been made in the German nomenclature in translating: the ending "-at" has been changed to "-ate," "ammin" becomes "ammine," and the names of the coordinated radicals are separated from one another and from that of the central atom by hyphens.

[2] B. Brauner, Z. anorg. Chem., **32**, 10 (1902).

[3] In some cases it is necessary to use the symbol (n) to denote that the new system of nomenclature is being used. Cf., A. Werner, "Neuere Anschauungen," p. 93.

[4] The "é" is accented so that it will not be mistaken for an English silent "e."

A few examples may make these rules clear:

$Na_3[Fe(CN)_6]'''$	=sodium hexacyano-ferriate;
$(NH_4)_3[ZnCl_5]'''$ [1]	=ammonium pentachloro-zincoate;
$[Cr(NH_3)_6] \cdots (NO_3)_3$ [2]	=hexammine-chromi nitrate;
$[Co(H_2O)_2(NH_3)_4] \cdots Cl_3$ [3]	=diaquo-tetrammine-cobalti chloride;
$[(NO_2)ClCo(en)_2] \cdot Br$ [4, 5]	=chloro - nitro - diethylenediamine-cobalti bromide;
$[Co(NO_2)_3(NH_3)_3]$ [6]	=trinitro-triammine-cobalt;
$[PtCl_2(NH_3)_2]$ [7]	=dichloro-diammine-platinum.

The last two compounds are examples of neutral complexes undissociated in water. This character is indicated by the nomenclature.

Molecular compounds which possess time-honored and clear names and relatively simple structures are not unnecessarily encumbered with names derived from this system of nomenclature. Sulphuric acid, $[SO_4]H_2$, would possess, according to this system, the unfamiliar name "tetroxo-sulphuron acid"; sodium thiosulphate, $[SSO_3]Na_2$, would become "sodium thio-trioxo-sulphuronate"; and perchloric acid, $[ClO_4]H$, "tetroxo-chlorin acid." (The endings *-on* and *-in* are used as an indication of the sexivalent or septivalent condition of the central atom.)

[1] C. Marignac, Ann. Min., [5] **12**, 1 (1857).
[2] S. M. Jörgensen, J. prakt Chem., [2] **30**, 6 (1884).
[3] S. M. Jörgensen, Z. anorg. Chem., **2**, 294 (1892).
[4] A. Werner and L. Gerb, Ber., **34**, 1743 (1901).
[5] The inconvenient formula $H_2N.CH_2.CH_2.NH_2$ is abbreviated to "en."
[6] S. M. Jörgensen, Z. anorg. Chem., **5**, 192 (1894); **13**, 175 (1897).
[7] S. M. Jörgensen, Z. anorg. Chem., **24**, 181 (1900); E. Biilmann and A. C. Andersen, Ber., **36**, 1570 (1903).

7. Addition Compounds

The large number of complex compounds may be divided, on the basis of their origin and structure, into two great groups, addition compounds and penetration [1] compounds.

As the name indicates, addition compounds result when a compound of the first order adds one or more molecules of another compound of the first order by means of auxiliary valencies. The atom of the first compound which manifests combining power until its coordination number has been satisfied becomes the central atom of the new complex compound. It is essential in this case that all the atoms originally bound to it be in "direct" union with it, or, in other words, that they be held in the nucleus. If the central atom cannot fulfil this condition, if it loses one of these atoms from the nucleus, the compound can no longer be classed as an addition compound.

Examples of such addition compounds have already been given. Along with the first example,

$$PtCl_4 + 2NH_3 = [PtCl_4(NH_3)_2],$$

we may place all other analogous compounds which result from the addition of neutral molecules, such as ammonia, to salts of the first order, such as $PtCl_4$, and which show by their very low conductivity in solution that all the groups previously existing as acid radicals are directly bound in such a manner as to be incapable of electrolytic dissociation. The fact that $[PtCl_4(NH_3)_2]$ is a non-electrolyte has been mentioned before.

The non-electrolyte $[Co(NH_3)_3(NO_2)_3]$, described previously,[2] is another typical example of an addition compound and belongs here also. In the case of cobaltic nitrite, $Co(NO_2)_3$, since the cobalt atom exerts its auxiliary valencies and reaches a coordination number of six, three molecules of the first order are added to form a complex, and all three nitrite radicals are held in direct union in the nucleus.

[1] There is no simple exact equivalent in English of the German "Einlagerungsverbindungen." The term "penetration compounds" is suggested as one which expresses clearly the denotation of the word.

[2] See p. 20.

We may cite trichloro-tripyridine-chromium $[Cr(Py)_3Cl_3]$ [1] as a corresponding chromium compound. Tetrachloro-dipyridine-tin $[Sn(Py)_2Cl_4]$ [2] also belongs to this class.

Furthermore, all the so-called "double salts," in which the anions unite in the nucleus with the central atom, are true addition compounds:

$$PtCl_4 + 2KCl = [PtCl_6]K_2$$

$$AuCl_3 + KCl = [AuCl_4]K$$

$$Co(NO_2)_3 + 3KNO_2 = [Co(NO_2)_6]K_3$$

$$Fe(CN)_3 + 3KCN = [Fe(CN)_6]K_3.$$

Finally, compounds of the higher order resulting from the union of two oxides belong in this class; among these compounds we are especially interested in addition products of oxides with water. Along with sulphuric acid, which was previously mentioned in this connection,

$$SO_3 + H_2O = [SO_4]H_2,$$

we find also:

$$CrO_3 + H_2O = [CrO_4]H_2$$
Chromic acid

$$MnO_3 + H_2O = [MnO_4]H_2$$
Manganic acid

$$SiO_2 + 2H_2O = [SiO_4]H_4$$
Orthosilicic acid

$$P_2O_5 + 3H_2O = 2[PO_4]H_3$$
Orthophosphoric acid

$$P_2O_3 + 3H_2O = 2[PO_3H]H_2$$
Orthophosphorous acid

$$Cl_2O_7 + H_2O = 2[ClO_4]H.$$
Perchloric acid

[1] P. Pfeiffer, Z. anorg. Chem., **24**, 283 (1900); **55**, 99 (1907).
[2] A. Werner and P. Pfeiffer, Z. anorg. Chem., **17**, 82 (1898).

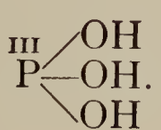
The agreement which all these acids show, in that they possess a maximum of four oxygen atoms in the nucleus, may be explained as follows:

The coordination number of the elements cited, with respect to oxygen, is four. Exceptions are found in the case of iodine and tellurium, which can form the acids $[IO_6]H_5$ [1] and $[TeO_6]H_6$, [2] respectively. Further, it must be emphasized that toward other elements another coordination number may be shown; in the case of silicon we find the compound $[SiF_6]H_2$. [3]

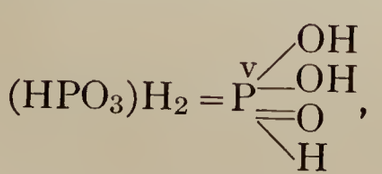
We shall now attempt to explain the uniform behavior of the oxygen acids by the assumption, from analogy with stereochemical phenomena which appear in the case of other compounds, that a certain spacial arrangement of the oxygen atoms exists and that there is no room, so to speak, for more than four atoms.

The constitutional formulæ based on the coordination theory possess a great advantage, because in direct contrast with those of the ordinary chemical valence theory they indicate clearly why the hydrogen atoms, standing in indirect combination, dissociate in solution and have the properties of ions. Also, the number of hydrogen ions is shown directly, a fact which the example of phosphorous acid illustrates strikingly.

This compound, formed by the reaction between PCl_3 and $3H_2O$, should certainly react as a tribasic acid according to the chemical valence formula



Since, however, only two hydrogen atoms are replaceable by metals,[4] it is given the unsymmetrical formula



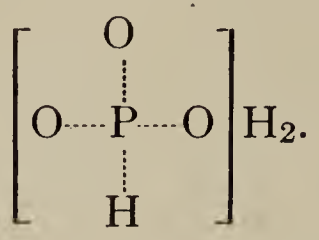
[1] H. L. Wells, Am. Chem. J., **26**, 278 (1901); E. Müller and O. Friedberger, Ber., **35**, 2652 (1902).

[2] E. B. Hutchins, Jr., J. Am. Chem. Soc., **27**, 1157 (1905).

[3] Gmelin-Kraut, Vol. III, Part 1, pp. 184, 1266.

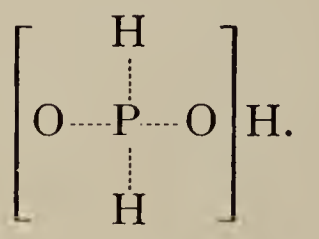
[4] A. Wurtz, Ann., **43**, 318 (1842); **58**, 49 (1846).

and is accordingly derived from quinquivalent phosphorus. This arbitrary assumption appears self-evident in the formulation according to the coordination theory:



The coordination number of phosphorus is four. Three coordination positions can be occupied by the oxygen atoms; hence one hydrogen atom in addition must enter the nucleus in order that the remaining affinity may be saturated. This atom thereby loses its reactivity and is no longer replaceable by metals.

If this theory is correct hypophosphorous acid, H_3PO_2, must possess the constitution



In accordance with the theory it is found that this acid is actually monobasic.[1]

8. Penetration Compounds[2]

a. General

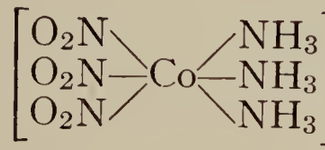
Reactivity is not always precluded by the union of two molecules of the first order, effected by the action of auxiliary valencies, with the formation of an addition compound. Under certain circumstances still other molecules may enter these compounds. A simple addition can, indeed, no longer take place, for we have explained that a compound is saturated by the occupation of all its coordination positions. Yet a union with other molecules is conceivable, if these penetrate into the molecule, compete for the positions of an equivalent number of radicals about the central atom, and expel them finally to posi-

[1] A. Wurtz, loc. cit.

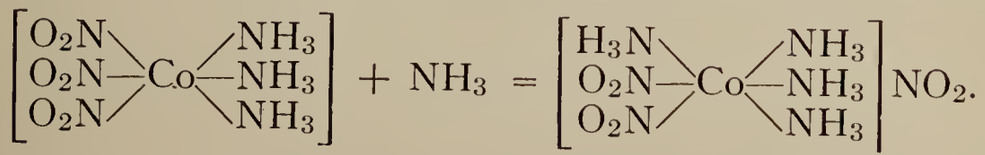
[2] See p. 27, footnote 1.

tions outside the central union. In this manner penetration compounds are formed. It is characteristic of this class of compounds that, in them, acid radicals which were previously incapable of becoming ions become loosely bound and therefore are split off as ions by dissociation in aqueous solution. The integer showing the number of molecules which has entered a compound before the first acid radical becomes an ion is called the ionizing auxiliary valence number.[1] An example may serve to make clear the process of formation of a penetration compound.

Cobaltic nitrite, $Co(NO_2)_3$, adds three molecules of ammonia with the formation of the addition compound $Co(NO_2)_3 \cdot 3NH_3$, to which, on the basis of our previous discussion, we assign the formula



In accordance with the direct method of linkage of the nitrite groups to the central atom, the compound is a very poor conductor of the electric current in aqueous solution. Trinitro-triammine-cobalt can be converted into a tetrammine compound by taking up another molecule of ammonia.[2] At the same instant, however, one of the nitrite groups is driven out of its position near the central atom to the second or outer sphere and thus becomes reactive; e.g., it can be set free as nitrous acid by dilute weak acids. At the same time the conductivity of the solution increases as a result of dissociation. The process of penetration must therefore take place according to the equation:



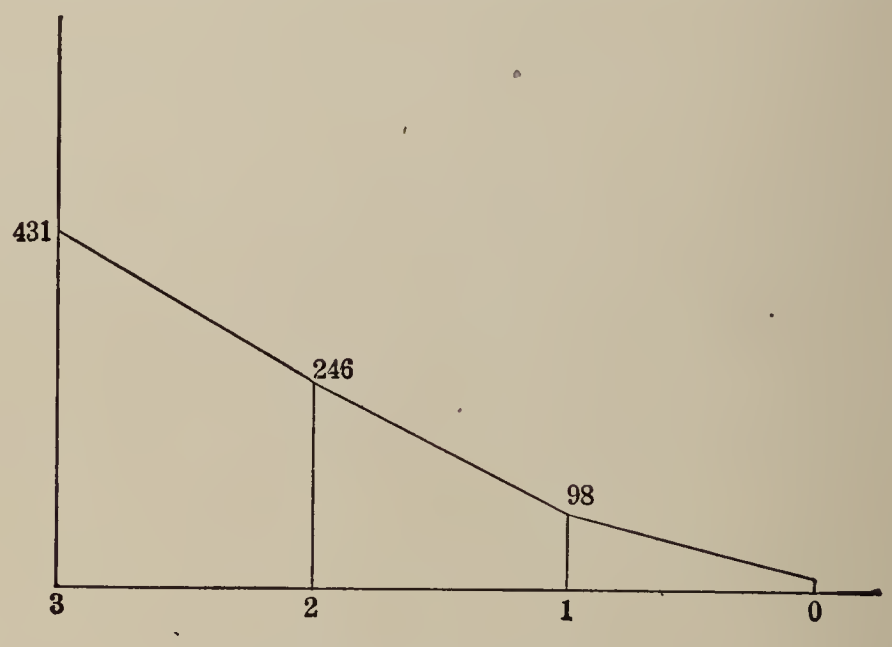
The ionizing auxiliary valence number is four in this case, because the first nitrite radical becomes an ion when the fourth ammonia molecule has entered the compound.

[1] A. Werner, "Neuere Anschauungen," pp. 196 ff.

[2] A. Werner and A. Miolati, Z. physik. Chem., **21**, 227 (1896). The preparation and properties of this particular compound are not given in the literature. See Gmelin-Kraut, Vol. V, Part 1, p. 403.

Since still other acid radicals remain in the central nucleus of this new penetration compound, it may be expected that these also can be displaced, one after another, by ammonia molecules. This is actually the case, and all the nitrite groups are finally displaced with the formation of a hexammine compound $[Co(NH_3)_6](NO_2)_3$. Then only is the power of reaction of the original compound, $[Co(NH_3)_3(NO_2)_3]$, exhausted.

From what has been said with regard to the first step in the penetration process, it is required that the other compounds formed by the successive displacement of nitrite radicals show a corresponding increase in electrical conductivity. That this requirement is satisfied experimentally may be seen from the following figure (Fig. 1). The value of the conductivity, increas-



0 = Trinitro-triammine-cobalt.[1]
1 = Dinitro-tetrammine-cobalti chloride.[2]
2 = Nitro-pentammine-cobalti chloride.[2]
3 = Hexammine-cobalti chloride.[2]

FIG. 1.—Molecular Conductivity at 1000 l. Dilution.

ing step by step, proves that more and more of the acid radicals are being held by ionizing linkages.

Many classes of inorganic compounds, for example, the ammine salts and hydrates, are classed as penetration compounds.

[1] A. Werner and A. Miolati, Z. physik. Chem., **12**, 48 (1893); **21**, 227 (1896).

[2] A Werner and A. Miolati, Z. physik. Chem., **14**, 506 (1894).

b. Metal Ammine Compounds

There is a large number of compounds of the general type $[\overset{III}{Me}(NH_3)_6]X_3$ corresponding to the compound hexammine-cobalti nitrite, which was used above as an example of the formation and formulation of penetration compounds. Chromium, iron, rhodium, and bismuth may function as $\overset{III}{Me}$, besides the metal cobalt, which has already been mentioned. All ammonia compounds built up according to the same scheme are called luteo-salts after the hexammine-cobalti salt, which was originally given this name because of its yellow color.

Among the chemical reactions of these compounds it is especially noteworthy that, just as in the case of simple salts, stronger acids liberate the anion in the form of the free weak acid, and further, that in this decomposition, even when concentrated sulphuric acid is used, the ammonia molecules are not removed from the complex nucleus.[1] This property is a particularly valuable confirmation of the constitutional formulæ given above, according to which the ammonia molecules are linked closely to the central atom while the acid radicals are more loosely bound in the outer sphere.

Besides the compounds derived from trivalent metals, there are also complexes with quadrivalent and bivalent central atoms, as, for example,

$[\overset{IV}{Pt}(NH_3)_6]Cl_4$,[2] $[\overset{IV}{Si}(NH_3)_6]Cl_4$, [3] $[\overset{IV}{Sn}(NH_3)_6]I_4$, [4] $[\overset{II}{Ni}(NH_3)_6]X_2$,

and the corresponding derivatives of cadmium, copper, iron, cobalt, and zinc.

As the formulæ show, the valence which a complex nucleus exerts toward the anions is the same as that which the central atom originally possessed. This fact is explained on the basis of the coordination theory by assuming that the auxiliary

[1] See p. 11.

[2] A. Werner and A. Miolati, Z. physik. Chem., **12**, 54 (1893).

[3] Persoz, Ann. chim. phys., **44**, 319 (1830); M. Blix and W. Wirbelauer, Ber., **36**, 4224 (1903).

[4] J. Personne, Compt. rend., **54**, 218 (1862).

valencies alone are called into play in holding the ammonia molecules in the inner sphere, and that the principal valencies—the ordinary valencies of the valence theory—remain available for radicals standing outside the nucleus.

In the hexammine salts the place of the ammonia molecules can be taken by other molecules related to ammonia, such as pyridine (C_5H_5N), ethylene diamine ($H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$), and hydrazine ($H_2N \cdot NH_2$).

In the metal ammine salts hitherto considered the coordination number was six, but there are also compounds of the type MeA_4 with the coordination number four, as, for example, the well-known cornflower blue compound of copper, $Cu(NH_3)_4SO_4$, [1] and further, $Zn(NH_3)_4Cl_2$ [2] and $\overset{II}{Pt}(NH_3)_4Cl_2$.

A large number of compounds of analogous constitution are derived from the hexammine salts by the successive replacement of one to six molecules of ammonia by acid radicals. The resulting types, which may be designated as

monacido-pentammine	$[\overset{III}{Me}(NH_3)_5X]X_2$
diacido-tetrammine	$[Me(NH_3)_4X_2]X$
triacido-triammine	$[Me(NH_3)_3X_3]$
tetracido-diammine	$[Me(NH_3)_2X_4]\overset{I}{Me}$
pentacido-monammine	$[Me(NH_3)X_5]Me_2$
hexacido	$[MeX_6]Me_3$,

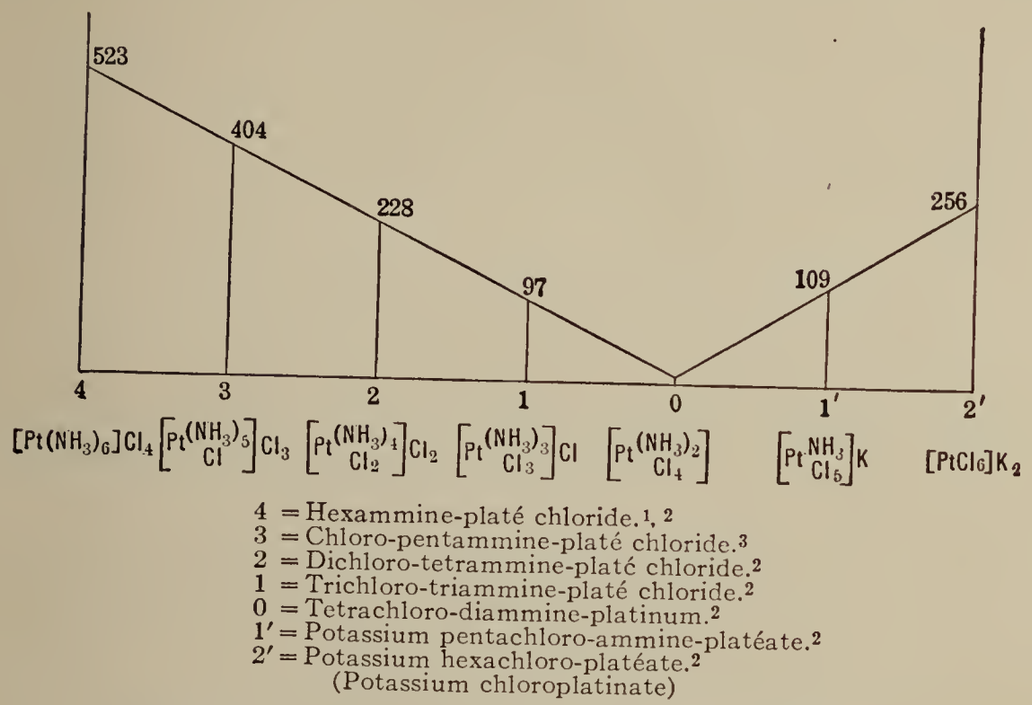
do not warrant separate consideration, since previous statements have clearly shown how their constitutions can be determined and whether they function in solution as neutral molecules, anions, or cations. The acid radicals generally found in them are

$$Cl,\ Br,\ NO_2,\ SO_4,\ SCN,\ CO_3,\ C_2O_4,\ SO_3,\ NO_3.$$

As an especially clear example of the step-by-step transformation of one group into another we may finally give a diagram

[1] I. Guareschi, Atti accad. sci. Torino, **32**, 193 (1896).
[2] A. A. Blanchard, *J.* Am. Chem. Soc., **26**, 1326 (1904).

of the molecular conductivities of the compounds of the platinum series (Fig. 2).



4 = Hexammine-platé chloride.[1, 2]
3 = Chloro-pentammine-platé chloride.[3]
2 = Dichloro-tetrammine-platé chloride.[2]
1 = Trichloro-triammine-platé chloride.[2]
0 = Tetrachloro-diammine-platinum.[2]
1′ = Potassium pentachloro-ammine-platéate.[2]
2′ = Potassium hexachloro-platéate.[2]
(Potassium chloroplatinate)

FIG. 2.—Molecular Conductivity at 1000 l. Dilution.

From this diagram it may be seen that the compounds, according to the number of acid radicals in the complex nucleus, are either non-electrolytes (triacido group) or electrolytes. The diagram also shows whether they are quaternary electrolytes, dissociating into four ions (hexacido group), ternary (monacido and pentacido groups), or binary (diacido and tetracido groups).

c. Hydrates

If we consider the great number of inorganic salts containing water of hydration, it is apparent that the number $6H_2O$ is especially common. This fact, which indicates a certain relationship with the hexammine salts, as well as the fact that the combining proportions in these molecular compounds—for the hydrates also belong to this class—can not be satisfactorily explained by the valence hypothesis, makes it quite apparent

[1] See footnote 4, p. 25.

[2] A. Werner and A. Miolati, Z. physik. Chem., **12**, 54 (1893); **14**, 506 (1894).

[3] L. Tschugaeff and N. Wladimiroff, Compt. rend., **160**, 840 (1915).

that coordination formulæ are also to be applied to these compounds. Therefore, salts such as $FeCl_3 \cdot 6H_2O$[1] may be formulated as complex salts:

$$[Fe(OH_2)_6]Cl_3.$$

We may mention here as additional examples:

$AlCl_3 \cdot 6H_2O$, [2] $NiCl_2 \cdot 6H_2O$, [3] $CoCl_2 \cdot 6H_2O$, [4]

$Zn(NO_3)_2 \cdot 6H_2O$, [5] $CaCl_2 \cdot 6H_2O$, [6] $MgCl_2 \cdot 6H_2O$. [7]

In all these hexahydrates the water molecules are located about the central atom in the first sphere, while the acid radicals are indirectly linked and are therefore split off as ions in solution.

That a close relationship between hexammines and hydrates must actually exist is seen from the fact that there are compounds containing both ammonia and water. The so-called roseo-salts of cobalt (beautiful red salts) are especially well known; they are derived from the hexammines by the replacement of one, two, or three ammonia molecules by water (aquo) and are therefore represented by the formulæ:

$[Co(NH_3)_5(OH_2)]Cl_3$ [8] = aquo-pentammine-cobalti chloride,

$[Co(NH_3)_4(OH_2)_2]Cl_3$ [9] = diaquo-tetrammine-cobalti chloride,

$[Co(NH_3)_3(OH_2)_3]Cl_3$[10] = triaquo-triammine-cobalti chloride.

In all these compounds we note that the coordination number (six) of the cobalt atom is satisfied by the simultaneous action of water and ammonia molecules. A proof of the assumption that the water is actually in the nucleus lies in the fact that, when the

[1] H. W. B. Roozeboom, Z. physik. Chem., **10**, 477 (1892).
[2] L. M. Dennis, Z. anorg. Chem., **9**, 339 (1895).
[3] O. L. Erdmann, J. prakt. Chem., **7**, 249 (1836).
[4] E. J. Mills, Phil. Mag., [4] **35**, 245 (1868).
[5] J. M. Ordway, Am. J. Sci. [2] **27**, 14 (1859).
[6] H. W. B. Roozeboom, Z. physik. Chem., **4**, 31 (1889).
[7] J. H. van't Hoff and W. Meyerhoffer, Z. physik. Chem., **27**, 75 (1898).
[8] S. M. Jörgensen, Z. anorg. Chem., **17**, 461 (1898).
[9] S. M. Jörgensen, ibid., **2**, 294 (1892).
[10] A. Werner, Ber., **39**, 2678 (1906).

water molecules are eliminated by heating, the acid radicals, which were previously capable of ionization, enter their positions. This conclusion is definitely proved by the decrease in conductivity and by the failure of the precipitation reaction. Compounds are thus formed, such as the violet-red purpureo-cobalti chloride (chloro-pentammine-cobalti chloride), according to the equation

$$[Co(NH_3)_5(OH_2)]Cl_3 - H_2O = [Co(NH_3)_5Cl]Cl_2.$$

In the resulting compound, $CoCl_3 \cdot 5NH_3$, only two chlorine atoms can be precipitated by silver nitrate. The manner of ionization has been described previously.[1]

An excellent contribution to the theory of hydrates is also furnished by chromic chloride ($CrCl_3 \cdot 6H_2O$), which is known in three isomeric forms.[2] The first form, grayish blue in color, holds all three chlorine atoms in aqueous solution in ionizable linkages, a fact which is proved by the complete precipitation with silver nitrate. Hence, according to our previous conceptions, it is given a formula analogous to that of the hexammine:

$$[Cr(OH_2)_6]Cl_3.$$

The second form, green chromic chloride, gives up only two chlorine atoms on precipitation with silver nitrate and is therefore to be regarded as

$$[Cr(OH_2)_5Cl]Cl_2 + 1H_2O.$$

Finally, the third isomer, likewise green, loses only one chlorine atom with silver nitrate, thereby showing its constitution to be

$$[Cr(OH_2)_4Cl_2]Cl + 2H_2O.$$

As an especially illuminating proof of the correctness of the hydrate theory we may also call attention to the fact that, with one exception, all the intermediate steps between chromic salt hydrates and ammine chromic complexes have been prepared.

[1] See p. 22.

[2] See pp. 45–46.

The close relationship, indicating a similar constitution, is seen at once from an examination of the following series; the gradual color change is also remarkable.

$$[Cr(NH_3)_6]X_3\ ^{1} \rightarrow [Cr(NH_3)_5(OH_2)]X_3\ ^{2}$$
Yellow — Orange yellow

$$\rightarrow [Cr(NH_3)_4(OH_2)_2]X_3\ ^{3} \rightarrow [Cr(NH_3)_3(OH_2)_3]X_3\ ^{4}$$
Orange red — Pale red

$$\rightarrow [Cr(NH_3)_2(OH_2)_4]X_3\ ^{5} \rightarrow [Cr(NH_3)(OH_2)_5]X_3$$
Violet red — Unknown

$$\rightarrow [Cr(OH_2)_6]X_3.\ ^{6}$$
Violet

In connection with the hydrate theory, we have next to consider the sulphates crystallizing with seven molecules of water, for example, $FeSO_4 \cdot 7H_2O$ [7] and $ZnSO_4 \cdot 7H_2O$. [8] From various facts, such as the dissociation tension of the salts, it is evident that the seventh molecule of water is held in a different linkage.[9] Therefore, in this case we arrive at the conclusion that six molecules of water are in the complex, and that the seventh, along with the sulphate radical, is in the outer sphere, as shown by the formula

$$[Fe(OH_2)_6]SO_4 + H_2O.$$

Greater difficulties exist in the correlation of hydrates containing a still larger number of water molecules. In the case

[1] S. M. Jörgensen, J. prakt. Chem., [2] **30**, 12 (1884).
[2] O. T. Christensen, ibid., [2] **23**, 28 (1881).
[3] P. Pfeiffer, Ber., **40**, 3130 (1907).
[4] A. Werner, ibid., **39**, 2667 (1906).
[5] A. Werner and J. Klien, ibid., **35**, 287 (1902).
[6] A. Werner and A. Gubser, ibid., **34**, 1591 (1901).
[7] Dammer, "Handbuch der anorganischen Chemie," III, 327–330; Enke (Stuttgart), 1893.
[8] Gmelin-Kraut, Vol. IV, Part 1, pp. 39–41, 619–622.
[9] In regard to hydrates apparently not in agreement with the hydrate theory, compare the discussion given in R. Weinland's "Einführung in die Chemie der Komplex-Verbindungen," pp. 286 ff.; Enke (Stuttgart), 1919.

of the alums this number is twelve. Here, in order to retain the compounds in the hexahydrate series, it is assumed that a double molecule, $(H_2O)_2$, occupies one coordination space.[1] Hence, potassium alum is given the formula

$$[Al(H_4O_2)_6](SO_4)(SO_4K).$$

This assumption is justified, inasmuch as ordinary water does not correspond to the monomolecular, but at least to the bimolecular formula. All that is lacking is a good explanation as to why water is monomolecular in the hexahydrates and bimolecular in the dodecahydrates.

9. Polyacids [2]

On page 15 it was shown that weak acids can also give rise to complex compounds, as do certain metals. Here there are two different possibilities to consider. In one case the positions of the oxygen atoms are occupied by the same acid radical, which is capable of forming complex acid radicals, while in the other case they are occupied by radicals of some other acid. According to this differentiation the resulting compounds may be classified as isopolyacids or as heteropolyacids.

In both groups there occurs a replacement of one or more oxygen atoms by acid radicals. For example, if each of the four oxygen atoms in chromic acid is replaced successively by the chromate radical, CrO_4, the following isopolyacids result:[3]

$$[CrO_4]H_2, \quad \left[\begin{matrix} & (CrO_4) \\ Cr & \\ & O_3 \end{matrix}\right]H_2, \quad \left[\begin{matrix} & (CrO_4)_2 \\ Cr & \\ & O_2 \end{matrix}\right]H_2, \quad \left[\begin{matrix} & (CrO_4)_3 \\ Cr & \\ & O \end{matrix}\right]H_2;$$

Chromic acid — Dichromic acid — Trichromic acid — Tetrachromic acid

some of the alkali salts of these isopolyacids are well-known compounds. Comparable with potassium bichromate or pyro-

[1] Cf., C. Schaefer and M. Schubert, Ann. Physik, **50**, 339 (1916); **55**, 397 (1918); L. Vegard and H. Schjelderup, ibid., **54**, 146 (1917).

[2] Cf., A. Rosenheim and J. Jänicke, Z. anorg. Chem., **100**, 304; **101**, 215, 235 (1917); P. Pfeiffer, ibid., **105**, 26 (1919).

[3] A. Miolati, J. prakt. Chem., [2] **77**, 444 (1908).

chromate are other pyroacids which may likewise be formulated as isopolyacids; thus we may perhaps assign to potassium pyrosulphate the following formula:

$$[SO_4]K_2+(SO_4)''-O=\left[\begin{matrix}(SO_4)\\ S\\ O_3\end{matrix}\right]K_2.$$

From the same point of view we may consider the polysilicic acids, from which are derived innumerable silicates occurring in nature.[1] By the addition of the metasilicate ion to a metasilicate we obtain the disilicate, $K_2Si_2O_5$:

$$[SiO_3]K_2+(SiO_3)''-O=\left[\begin{matrix}(SiO_3)\\ Si\\ O_2\end{matrix}\right]K_2.$$

However, very little is known at the present time regarding the actual constitution of these polyacids.[2]

A few examples of heteropolyacids, of which many are known, have already been mentioned.[3] We shall now consider briefly two well-known compounds of this type—phosphomolybdic and silicotungstic acids.[4]

The fact that in these, and also in most of the similar polyacids, twelve acid radicals at most enter another molecule,

$$(NH_4)_3PO_4\cdot 12MoO_3\cdot 6H_2O,$$

$$SiO_2\cdot 12WO_3\cdot 4H_2O,$$

leads, on the basis of the coordination theory, to the assumption that here also the coordination number (six) of the central atom gives rise to a similar regularity, since steric hindrance prevents the entrance of more than six double molecules. Following out this idea, we choose as the basis of the corresponding

[1] B. P. Groth, "Tabellarische Uebersicht der Mineralien"; Z. B. C. Dölter, "Mineralchemie"; E. Jordis, Z. anorg. Chem. since 1905; P. Niggli, recent numbers of Z. anorg. Chem.

[2] Cf., R. Schwarz and H. Bausch, Ber., **54**B, 802 (1921).

[3] See p. 15.

[4] P. Pfeiffer, Z. anorg. Chem., **105**, 26 (1919).

complexes, acids of such a nature that, upon the addition of water, they contain six oxygen atoms coordinated with the central atom; thus, as the formulæ show, they form hexoxo acids:

$$[SiO_4]H_4 + 2H_2O = [SiO_6]H_8,$$

$$[PO_4]H_3 + 2H_2O = [PO_6]H_7.$$

In these compounds the oxygen atoms can be replaced, either completely or partly, by radicals of other acids, as, for example, Mo_2O_7 or W_2O_7, the anions of pyromolybdic and pyrotungstic acids respectively. Hence, by complete replacement of the oxygen atoms the following heteropolyacids result:

$$[Si(W_2O_7)_6]H_8,$$

Silicotungstic acid

$$[P(Mo_2O_7)_6]H_7.$$

Phosphomolybdic acid

As an example of an acid in which all the oxygen atoms of the nucleus have not been replaced, we may point out arsenomolybdic acid,[1]

$$\left[\begin{matrix} & (Mo_2O_7)_5 \\ As & \\ & O \end{matrix}\right] H_7.$$

The correctness of this formula is proved by the fact that the acid is actually heptabasic, since guanidine arsenomolybdate has the formula: [1]

$$\left[\begin{matrix} & (Mo_2O_7)_5 \\ As & \\ & O \end{matrix}\right] (CN_3H_6)_7.$$

[1] A. Rosenheim and A. Traube, Z. anorg. Chem., **91**, 75 (1915).

CHAPTER III

ISOMERISM OF THE COMPLEX COMPOUNDS

THE phenomenon shown by two compounds which have identical (empirical) chemical compositions but possess different properties, both from the chemical and physical points of view, is termed isomerism. This dissimilarity depends upon a difference in the inner structures of the compounds and usually impresses itself especially sharply on the physical properties; thus, the color, solubility, and melting- or boiling-points may diverge considerably. Since the general composition, as stated, is the same, naturally the chemical differences are usually slight.

While two substances which have identical chemical and physical properties must be considered identical, the case of two substances of the same composition but with different properties falls under isomerism. The identity holds, of course, only for the empirical formula obtained by analysis; the inner structures or constitutions must be different.

The variation in properties of isomeric compounds is attributed to different causes. To begin with, we may distinguish between two main groups: in the first case the molecular magnitudes are different, i.e., the numbers of individual atoms in the molecule are different, and this phenomenon is called polymerism; in the second case the molecular magnitudes are the same, but the arrangement of the atoms in the molecule is different. In this case we speak of isomerism in the narrow sense, or metamerism.

1. POLYMERISM

An especially apparent case of polymerism may be taken from organic chemistry. Two substances of the composition 92.25 per cent carbon and 7.75 per cent hydrogen are known,

from which data the simplest formula is found to be CH. The bimolecular derivative of this hypothetical basal compound is acetylene, C_2H_2, and the hexamer, C_6H_6, is benzene.

Some simple cases of polymerism among inorganic compounds will now be mentioned. Silver cyanide obtained from $K[Ag(CN)_2]$ according to the equation

$$K[Ag(CN)_2]+H_2SO_4=KHSO_4+AgCN+HCN$$

is monomolecular. A bimolecular polymer results from the reaction between this same complex salt and silver nitrate:[1]

$$K[Ag(CN)_2]+AgNO_3=Ag[Ag(CN)_2]+KNO_3.$$

To this class belong also the polymers of $NaPO_3$, sodium metaphosphate: $(NaPO_3)_2$, $(NaPO_3)_3$, and still higher polymers.[2]

Exactly similar polymerization phenomena exist among inorganic complex salts and are especially well known in the case of the metal ammine compounds. As an example, trinitro-triammine-cobalt, of which polymers have been prepared up to the pentamolecular compound, may be mentioned here.

$[Co(NO_2)_3(NH_3)_3]_1$ [3] = Trinitro-triammine-cobalt,

$[Co(NO_2)_3(NH_3)_3]_2$ [4] = $[Co(NH_3)_6]\cdots[Co(NO_2)_6]'''$,

$[Co(NO_2)_3(NH_3)_3]_3$ [5] = $[Co(NO_2)(NH_3)_5]\cdot\cdot[Co(NO_2)_4(NH_3)_2]_2'$,

$[Co(NO_2)_3(NH_3)_3]_4$ [6] = $[Co(NH_3)_6]\cdots[Co(NO_2)_4(NH_3)_2]_3'$,

$[Co(NO_2)_3(NH_3)_3]_5$ [7] = $[Co(NO_2)(NH_3)_5]_3\cdot\cdot[Co(NO_2)_6]_2'''$.

[1] J. Wagner, Chem. Ztg., **26**, 942 (1902).

[2] Gmelin-Kraut, Vol. II, Part 1, pp. 401–405.

[3] W. Gibbs, Proc. Amer. Acad., **10**, 14 (1874); S. M. Jörgensen, Z. anorg. Chem., **5**, 192; **7**, 302 (1894); **13**, 175 (1897); **17**, 475 (1898).

[4] S. M. Jörgensen, Z. anorg. Chem., **5**, 177 (1894).

[5] W. Gibbs, Proc. Amer. Acad., **10**, 31 (1874); S. M. Jörgensen, Z. anorg. Chem., **5**, 180 (1894).

[6] W. Gibbs, Proc. Amer. Acad., **11**, 34 (1876); S. M. Jörgensen, Z. anorg. Chem., **5**, 179 (1894).

[7] W. Gibbs, Proc. Amer. Acad., **11**, 8 (1876); S. M. Jörgensen, Z. anorg. Chem., **5**, 178 (1894).

The existence of the higher polymers is due to the fact that cobalt complexes, which can be either anions or cations according to the number and character of the coordinated molecules and acid radicals, form salts with one another which are to be considered as cobalt salts of cobalt acids.

In the case of chromium compounds, also, an analogous polymerization is known, since the polymers of $[Cr(NH_3)_3(SCN)_3]$ up to the pentamolecular form have been prepared.[1]

2. Coordination Isomerism

Coordination isomerism, which is characterized by a different distribution of the coordinated components, is in close relationship to polymerism of the type which we have just discussed. The phenomenon may be illustrated by the following general formulation:

$$[MeA_6][Me'X_6] \text{ isomeric with } [Me'A_6][MeX_6],$$

in which A represents a neutral substance, such as ammonia, and X a negative acid radical. Examples of this type are:

$$[Co(NH_3)_6] \cdots [Cr(CN)_6]''' \ ^{2}$$

Hexammine-cobalti hexacyano-chromiate

isomeric with

$$[Cr(NH_3)_6] \cdots [Co(CN)_6]'''. \ ^{3}$$

Hexammine-chromi hexacyano-cobaltiate

In place of $(CN)_6$ we may also have $(C_2O_4)_3$ (oxalato-),[4] and instead of $(NH_3)_6$, $(en)_3$ (ethylene diamine). The isomeric series may be differentiated visually by their colors, the cobalti salts being brown and the cobaltiates green.

Furthermore, we have the case of a different distribution of the components, the central atoms being the same, according to the following formulation:

$$[MeA_6]\,[MeX_6] \text{ isomeric with } [MeA_4X_2]\,[MeA_2X_4].$$

[1] A. Werner and J. Jovanovits, unpublished researches. See A. Werner, "Neuere Anschauungen," p. 330.

[2] P. Pfeiffer and M. Haimann, Ann., **346**, 73 (1906).

[3] S. M. Jörgensen, J. prakt. Chem., [2] **30**, 31 (1884).

[4] "Oxalato-" is often abbreviated to "oxalo-."

As an example of this type we may cite the compound hexammine-chromi trioxalato-chromiate,

$$[Cr(NH_3)_6] \cdots [Cr(C_2O_4)_3]''', \text{ [1]}$$
Green

and its coordination isomer oxalato-tetrammine-chromi dioxalato-diammine-chromiate,

$$[Cr(NH_3)_4(C_2O_4)]\cdot[Cr(NH_3)_2(C_2O_4)_2]'. \text{ [2]}$$
Orange

3. Hydrate Isomerism

This kind of isomerism is due to the fact that, in two or more compounds of identical empirical formulæ, water molecules may be held in different linkages.

In considering the theory of hydrates,[3] we became acquainted with chromic chloride, which crystallizes with six molecules of water. Different isomers of this compound exist, as has already been indicated, their constitutions being clearly shown by their different behavior in aqueous solution. The first isomer [4] is obtained when a chromic sulphate solution, prepared in the cold, is treated with a quantity of barium chloride solution sufficient for the complete precipitation of the sulphate radical. A violet solution of chromic chloride is formed in which all three chlorine atoms are present as ions, a fact which may be recognized upon precipitation with silver nitrate and which may be shown quantitatively by determination of the conductivity. Hence, according to the hydrate theory, it is hexaquo-chromi chloride,

$$[Cr(OH_2)_6]Cl_3.$$

In the solid state the salt is violet.

[1] P. Pfeiffer and S. Basci, Ann., **346**, 49 (1906).

[2] P. T. Cleve, Kong. Vet. Akad. Handl., **6**, No. 4, p. 24 (1865); P. Pfeiffer and S. Basci, Ann., **346**, 48 (1906).

[3] See p. 37.

[4] A. Recoura, Compt. rend., **102**, 548 (1886); Ann. chim. phys., [6] **10**, 34 (1887); A. Werner and A. Gubser, Ber., **34**, 1591 (1901).

If the above-described violet solution is boiled, the color becomes changed to green. If the cooled solution is then treated with silver nitrate, only one of the three chlorine atoms precipitates.[1] The other two can not be precipitated because they now belong to the nucleus. The constitutional formula of the new compound must therefore be written

$$[Cr(OH_2)_4Cl_2]Cl(H_2O)_2.$$

This shows that two water molecules are driven out of the nucleus by the entrance of two chlorine atoms and that, consequently, there is present only a univalent cation, to which one chlorine ion corresponds as the anion. Besides this ion, two water molecules are outside the nucleus in indirect linkage. In the solid state the salt forms emerald green crystals.

A third isomer,[2] also green, can be obtained, along with the hexaquo salt, from a solution of dichloro-tetraquo-chromi chloride by boiling and subjecting it to the action of hydrogen chloride gas. From the behavior of the solution, which is bluish-green, toward silver nitrate, and from the conductivity, it is found that the compound present is monochloro-pentaquo-chromi chloride,

$$[Cr(OH_2)_5Cl]Cl_2(H_2O),$$

in which only two chlorine atoms are in ionizable linkages, while five water molecules and one chlorine atom are in the complex nucleus.

As another characteristic example of this type of isomerism, both salts of the formula

$$Cr(en)_2(H_2O)_2Br_3$$

may be considered. They are noticeably different in appearance, since one is brownish-orange and the other violet-red.

[1] E. Peligot, Ann. chim. phys., [3] **12**, 537 (1844); L. Godefroy, Compt. rend., **100**, 105 (1885); A. Recoura, ibid., **102**, 515 (1886); A. Werner and A. Gubser, Ber., **34**, 1594 (1901); N. Bjerrum, Z. physik. Chem., **59**, 339 (1907).

[2] N. Bjerrum, Ber., **39**, 1599 (1906); Z. physik. Chem., **59**, 596 (1907).

All the bromine is precipitated from an aqueous solution of the orange salt by silver nitrate.[1] We assign to it the formula

$$[Cr(en)_2(OH_2)_2]Br_3.$$

Diaquo-dien-chromi bromide

Silver nitrate precipitates only two-thirds of the total bromine from a solution of the violet isomer; hence, one atom of bromine must be held in the complex. This behavior corresponds to the formula

$$[Cr(en)_2(OH_2)Br]Br_2(H_2O).$$ [2]

Bromo-aquo-dien-chromi bromide

4. Ionization Isomerism

As has been stated several times, acid radicals—such as $=[SO_4]$, $-Cl$, $-Br$, $-NO_3$—lose their typical ionic properties as soon as they are linked in the first sphere of a complex nucleus. The characteristic precipitations of analytical chemistry fail, and a stronger acid, contrary to the usual rule, may be unable to free a weaker acid, or, at least, sets it free only with difficulty. If two different acid radicals, x and y, occur in a complex compound, either x or y may be a part of the nucleus. In aqueous solution, naturally, only one of the two radicals will be split off as an ion, in the first case y, in the second, x. Two compounds of this type, of the same composition but giving different ions in solution, are said to be ionization isomers.

The following formulæ illustrate the phenomenon:

$[MeA_5x]y$ is the ionization isomer of $[MeA_5y]x$.

For example, two salts of the formula $Co(NH_3)_5Br(SO_4)$ are known, one violet and the other red. The first gives SO_4'' ions in solution, since they can be precipitated by $Ba^{\cdot\cdot}$ ion, and it is therefore

$$[Co(NH_3)_5Br]^{\cdot\cdot}\ SO_4''$$; [3]

Bromo-pentammine-cobalti sulphate

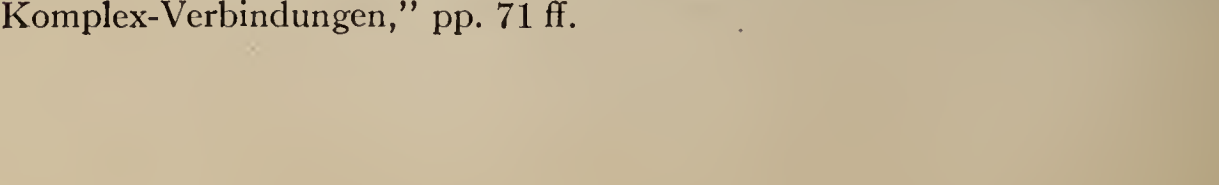
[1] P. Pfeiffer, Ber., **40**, 3836 (1907); Z. anorg. Chem., **58**, 242 (1908).
[2] P. Pfeiffer, Ber., **40**, 3832 (1907).
[3] S. M. Jörgensen, J. prakt. Chem., [2] **19**, 63 (1879).

a solution of the second gives the test for the bromine ion and this salt is therefore the bromide

$$[Co(NH_3)_5(SO_4)] \cdot Br'.$$ [1]

Sulphato-pentammine-cobalti bromide

To bring this important fact once more to attention, this compound gives confirmation of the fact that even a bivalent radical, like SO_4, sometimes occupies only one coordination position in a complex nucleus. However—and this point should be emphasized—a bivalent radical always requires two principal valencies of the central atom; sulphato-pentammine-cobalti ion is only univalent; i.e., two of the three principal valencies of the cobalt have already been saturated by the sulphate radical:



An additional illustration of ionization isomerism is found in

$[Co(NH_3)_4Cl(NO_2)]Cl$ [2] and $[Co(NH_3)_4Cl_2]NO_2$. [3]

Chloro-nitro-tetrammine-cobalti chloride — Dichloro-tetrammine-cobalti nitrite

In the case of chromium salts, also, a similar phenomenon is observed:

$[Cr(OH_2)_5Cl]SO_4$ [4] isomeric with $[Cr(OH_2)_5(SO_4)]Cl$. [5]

Chloro-pentaquo-chromi sulphate — Sulphato-pentaquo-chromi chloride

5. Stereoisomerism [6]

A large number of complex compounds of cobalt, chromium, and platinum exhibit the phenomenon of isomerism although no difference in the structure of the two isomers can be identified,

[1] S. M. Jörgensen, J. prakt. Chem., [2] **31**, 270 (1885).

[2] S. M. Jörgensen, Z. anorg. Chem., **5**, 193; **7**, 290 (1894).

[3] A. Werner and A. Klein, ibid., **14**, 35 (1897).

[4] A. Recoura, Bull. soc. chim., [3] **27**, 1156 (1902); R. Weinland and R. Krebs, Z. anorg. Chem., **48**, 251 (1906); R. Weinland and T. Schumann, Ber., **40**, 3091 (1907).

[5] R. Weinland and T. Schumann, Z. anorg. Chem., **58**, 176 (1908).

[6] See A. Werner, "Neuere Anschauungen," pp. 351 ff.; R. Weinland, "Komplex-Verbindungen," pp. 71 ff.

either on the basis of electrolytic dissociation or of analytical behavior, as polymerism or any of the other types of isomerism discussed previously. Since a different structure cannot be assigned to them from their chemical behavior, they are said to be structurally identical. Yet it is perfectly evident, from differences in color, that some kind of dissimilarity must exist.

Although in these cases a structurally isomeric formulation is impossible, a difference in the structure of the isomers is conceivable if the arrangement of the individual components of the molecule varies in regard to spacial relations. A difference of this kind, of course, would not be apparent in a formula constructed in the plane of the paper.

If one thinks of a metal ammine compound with the coordination number six, $[Co(NH_3)_6]Cl_3$ for example, as a geometric figure, the simplest supposition is that all six coordinated groups lie in equivalent positions at equal distances from the central atom. The octahedral arrangement fulfils this condition if we consider the central atom to be placed in the center and the other components at the corners of the octahedron.

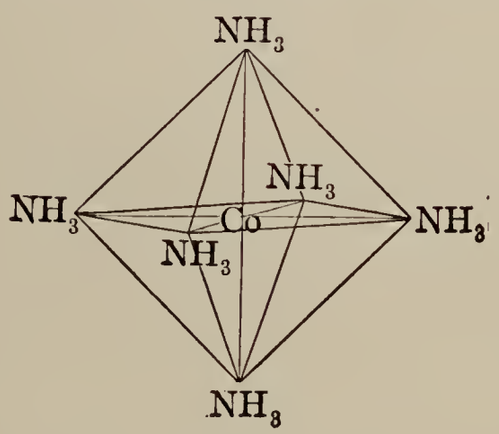


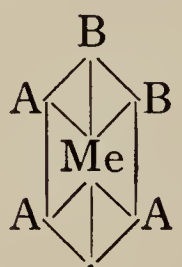
Fig. 3.

The radicals in indirect union, which are split off as ions in solution, need not be taken into consideration. Their conduct as a whole indicates that they have no influence whatsoever on the structure of the nucleus, but that they are linked to the complex in some looser manner, not to be defined more definitely, which permits them great freedom of motion.

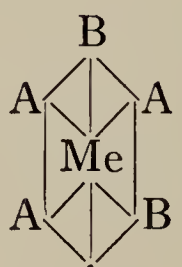
This primary, purely theoretical assumption of the octahedral structure for a large class of inorganic complex compounds

secures a firm footing from two facts: first, all the phenomena of isomerism hitherto unexplained become reconciled by its help; and second, up to this time no phenomena contrary to it, and necessitating another method of explanation, have been observed. On the other hand, a number of isomeric compounds predicted on the basis of this hypothesis have actually been prepared synthetically.[1]

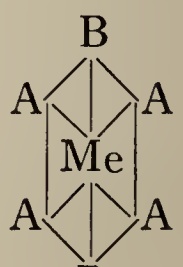
In explaining the phenomena of isomerism which we are considering, it appears feasible to assume that the six groups are arranged in a plane configuration, as in the benzene ring. If this assumption were correct, for a compound of the general type MeA_4B_2, just as for a benzene derivative of the type $C_6H_4R_2$, three isomers, as shown in the formulæ, would be possible, namely, *ortho*, *meta*, and *para*.



Ortho

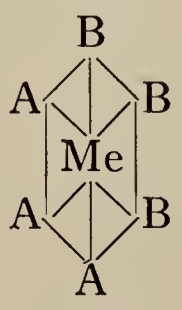


Meta



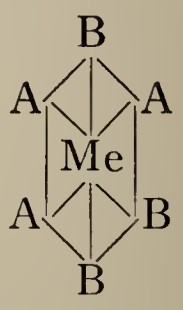
Para

Similarly, there would be three isomers of a compound of the type MeA_3B_3.



Adjacent

Symmetrical



Unsymmetrical

Since it has not been possible in any case to obtain three isomers of compounds corresponding to the two types mentioned,

[1] The recent work on crystal structure also supports the theory of octahedral arrangement. See R. Weinland, "Komplex-Verbindungen," pp. 417–420. See also: R. W. G. Wyckoff, recent numbers of J. Am. Chem. Soc.; R. G. Dickinson, ibid.; P. Scherrer and P. Stoll, Z. anorg. Chem., **121**, 319 (1922).

and since, in many cases, two isomers can be prepared, it seems certain that only the theory of spacial arrangement agrees with the actual conditions.

In the following pages, when we ascribe space formulæ to metal ammine compounds, we shall always have in mind the octahedral figure described above. However, for the sake of clearness, we shall choose the following simplified form and omit the symbol of the central atom. The individual corners of the octahedron are indicated by numbers from 1 to 6, according to the arrangement in Fig. 4.

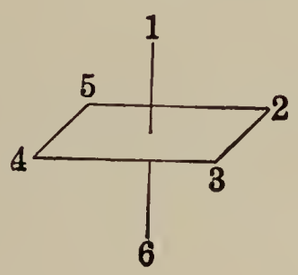


FIG. 4.

a. Stereoisomerism of the Series MeA_4B_2

If, as a concrete example, we now apply our space formula to the three cobalt ammines

$[Co(NH_3)_6]$, I $\qquad$ $[Co(NH_3)_5(NO_2)]$, II $\qquad$ $[Co(NH_3)_4(NO_2)_2]$, III

Formula I gives the space structure shown in Fig. 5.

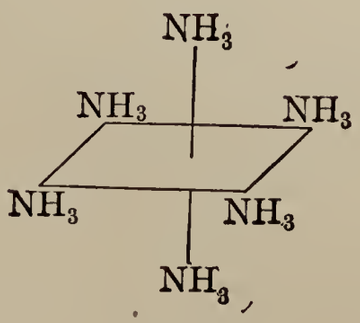


FIG. 5.

Formula II gives

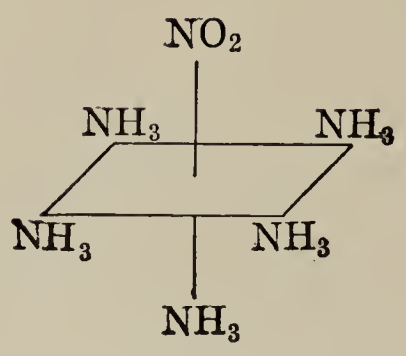
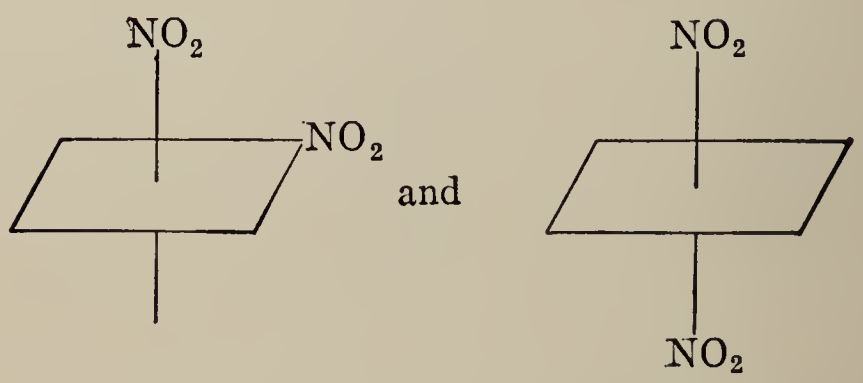


FIG. 6.

in which the position of the nitrite radical is immaterial. From Formula III we can secure two configurations.



1, 2-Dinitro- 1, 6-Dinitro-

FIG. 7.

This is the first conceivable case of stereoisomerism, and two salts [1] of the formula $[Co(NH_3)_4(NO_2)_2]$ actually exist—a brown form, called the flavo-salt, and a yellow form, the croceo-salt. Which of the two is the 1, 2- and which the 1, 6- cannot yet be stated. This question will be answered later, in the section on determination of configuration. At the present time we are concerned only with the fact that in one salt the nitrite radicals stand in neighboring positions, also called cis-positions, and in the other, in separated or trans-positions. Instead

[1] W. Gibbs, Proc. Amer. Acad., **10**, 2 (1874); S. M. Jörgensen, Z. anorg. Chem., **5**, 162 (1894).

of cis- or trans-positions, we may also speak of edge- (1, 2) and axial- (1, 6) substitution.[1]

Besides the dinitro-tetrammine-cobalti compound just given as an example, there is a large number of cobalt and chromium compounds of analogous composition, of which a selection will be mentioned here.

The replacement of four ammonia molecules by two bivalent ethylene diamine molecules, $H_2N \cdot CH_2 \cdot CH_2 \cdot NH_2$ (abbreviated to " en "), gives rise to dinitro-diethylenediamine-cobalt salts:

$$[(O_2N)_2Co(en)_2]X.\ ^{2}$$

These also exist in flavo- and croceo-series.

If the nitrite radicals bound in the complex are replaced by chlorine or bromine, violet-colored salts of the violeo-series and green salts of the praseo-series result; examples are known for cobalt as well as for chromium:

$$[Cl_2Cr(en)_2]X\ ^{3} \quad \text{and} \quad [Cl_2Co(en)_2]X.\ ^{4}$$

[1] The study of the stereochemistry of the complex compounds will be simplified by the use of stereochemical models. These consist of small cork stoppers or discs and a number of pins, with glass heads of different colors, such as are often used for locating points on maps. The corks represent the central atoms. Six pins are stuck into each, in the form of an octahedron. Molecules, such as ethylene diamine, which occupy two coordination positions may be represented by a doubly bent wire. The resulting models have the following appearance.

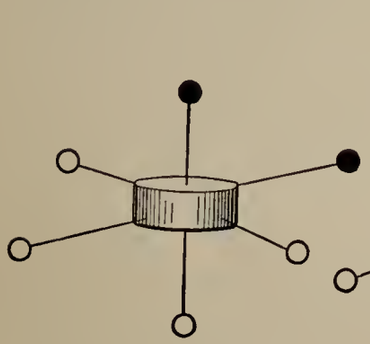


Fig. 8.

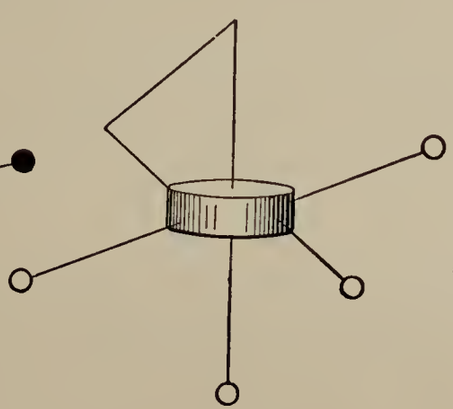


Fig. 9.

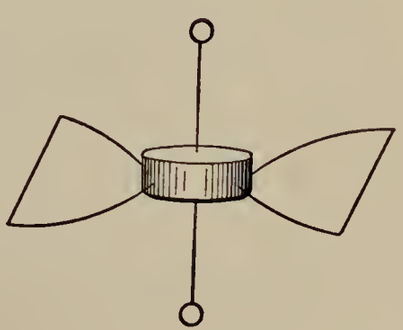


Fig. 10.

[2] A. Werner and E. Humphrey, Ber., **34**, 1720, 1726 (1901).
[3] P. Pfeiffer and G. Lando, Ber., **37**, 4275 (1904).
[4] S. M. Jörgensen, J. prakt. Chem., [2] **41**, 440 (1890).

If the thiocyanate radical (SCN) takes the place of chlorine or bromine, in the case of chromium the reddish-orange or yellowish-orange dithiocyanato-dien salts result:

$$[(SCN)_2Cr(en)_2]X;^{1}$$

and if water groups replace the acid radicals, the similarly colored diaquo-dien salts:

$$[(H_2O)_2Cr(en)_2]X_3.$$

The methods by which individual members of the isomeric series can be prepared will be discussed later. We shall now turn to the question of how it is possible to assign to each stereoisomer a definite space formula, or, in other words, how to determine whether the 1, 2- or edge-positions are occupied by the flavo- or the croceo-salt, by the violeo- or the praseo-salt.

Determination of Configuration (MeA_4B_2)

Cis-trans-isomerism was originally discovered among organic compounds. A short discussion of the phenomena connected with it in organic chemistry will facilitate the comprehension of the stereochemistry of inorganic compounds.

A simple example of this kind of isomerism is found in fumaric and maleic acids,[2] both of the formula HOOC·CH : CH·COOH. A molecule of this composition can be constructed in two spacially different forms, namely:

$$\begin{array}{l} HC\cdot COOH \\ \| \\ HC\cdot COOH \end{array} \quad \text{and} \quad \begin{array}{l} HOOC\cdot CH \\ \| \\ HC\cdot COOH \end{array}.$$

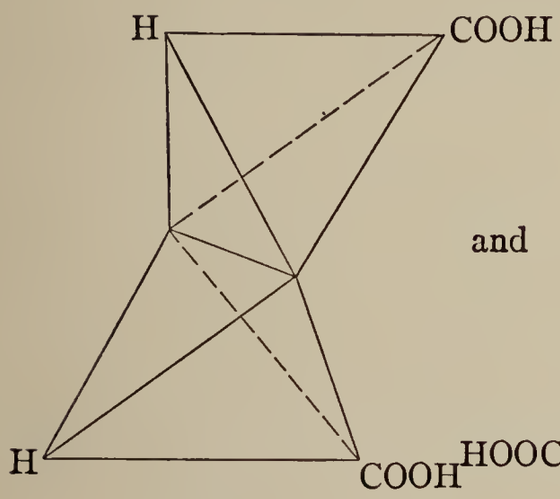
Cis Trans

That the two forms are not identical, i.e., that they can not be made congruent unless the doubly linked carbon atoms can be rotated through 180° with respect to each other, becomes evident from a spacial representation with tetrahedra, which

[1] P. Pfeiffer and P. Koch, Ber., **37**, 4268 (1904).

[2] See A. W. Stewart, "Stereochemistry," 2nd Ed., Chapter XII; Longmans (London), 1919.

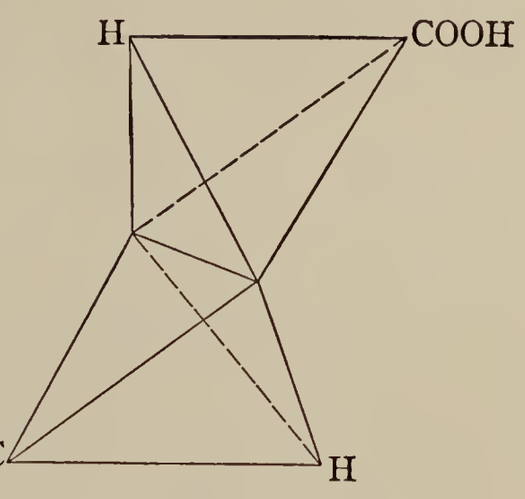
serve as the embodiment of the valencies of the quadrivalent carbon atom. Because of the double bond, the molecule becomes, so to speak, a rigid system.



I

Fig. 11.

and

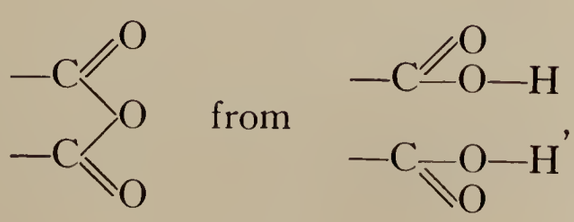


II

Fig. 12.

The decision as to which formula belongs to maleic acid and which to fumaric is reached from a study of their different chemical properties. Maleic acid has the power of forming an anhydride, while fumaric acid does not possess this property. Since the anhydride is formed by a reaction between the two carboxyl groups with the elimination of water, it can be deduced that this reaction is possible only when the two carboxyl groups are in adjacent positions, and that, therefore, Formula I belongs to the anhydride-forming maleic acid molecule. On the basis of this phenomenon of isomerism, the cis-configuration is generally designated as the " maleinoid " form and the trans- as the " fumaroid."

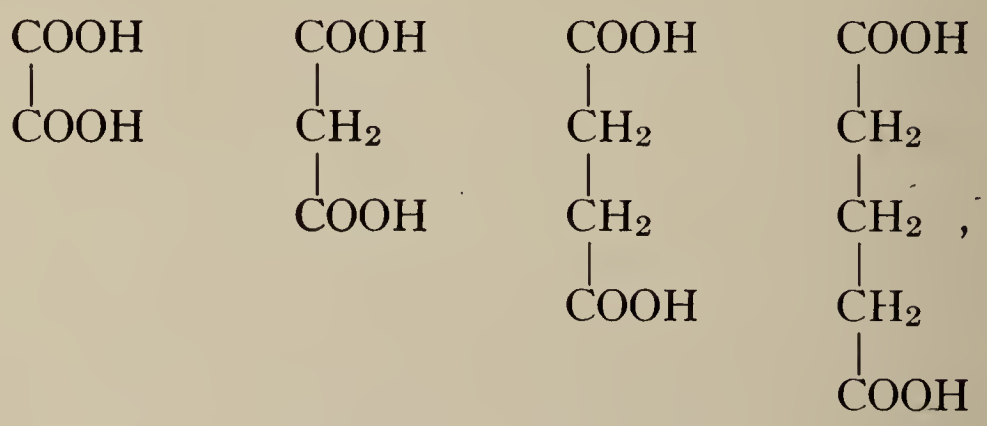
The occurrence, between spacially adjacent groups, of reactions leading to a so-called ring formation, as, in the preceding case, the formation of



from

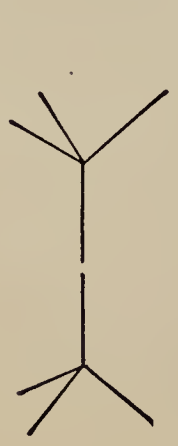
is frequently observed in organic chemistry; the fact that this type of reaction is so common supports the explanation.

Another typical example of such ring closure will be discussed briefly. Of the dicarboxylic acids—oxalic, malonic, succinic, and glutaric acids—only the last two are capable of forming anhydrides. If we represent their structural formulæ,



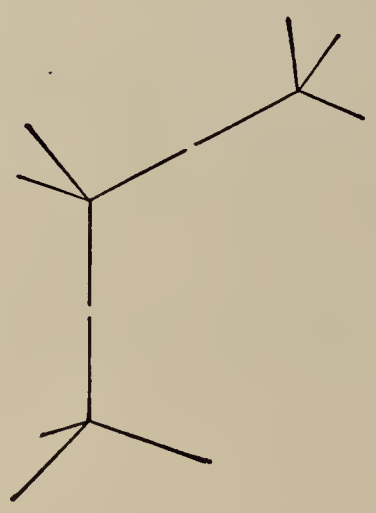
Oxalic acid Malonic acid Succinic acid Glutaric acid

it will certainly seem at first that in oxalic and malonic acids the two carboxyl groups are in close proximity to each other and therefore that ring closure should take place more easily in them than in the others. If, however, tetrahedral formulæ are used, the error of such an assumption is apparent. These formulæ show that in the acids with four or five carbon atoms the carboxyl groups are much closer to each other than in the lower homologues.



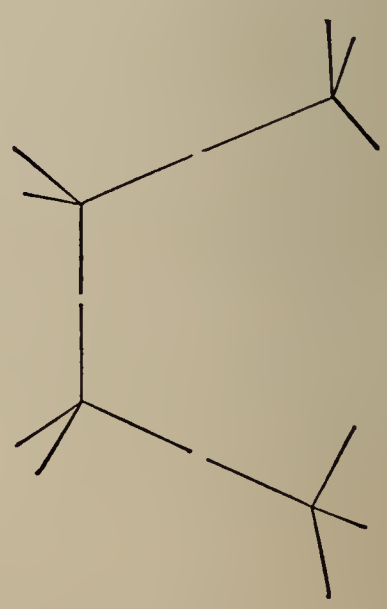
Oxalic acid

FIG. 13.



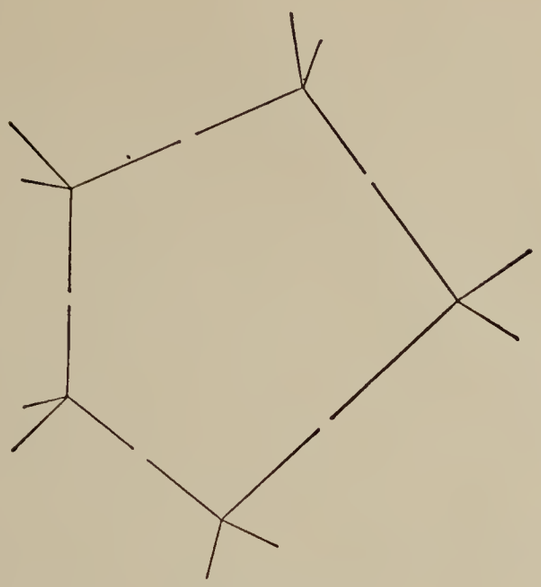
Malonic acid

FIG. 14.



Succinic acid

FIG. 15.

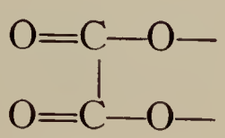


Glutaric acid

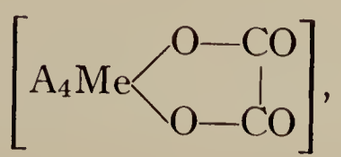
FIG. 16.

These ideas, which were established in the chemistry of carbon compounds, were then transferred by Werner to the subject of inorganic stereoisomerism.

There are certain series of complex metal salts, such as the oxalato and carbonato salts, in the origin of which it must be assumed that there is a kind of ring formation. If the oxalate radical



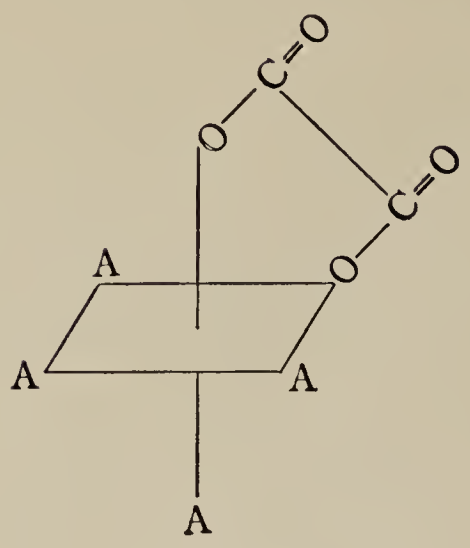
unites with the central atom of a complex nucleus to form



it is clear that we are dealing with a case of ring closing.

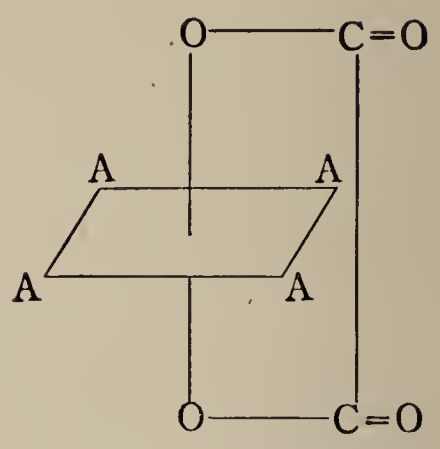
Which positions around the central atom—two adjacent, or two spacially separated, axial positions—are occupied by the two oxygen atoms?

Because of the analogy to organic compounds, we decide without hesitation upon the neighboring positions and prefer Formula I to Formula II, which is apparently very much strained.



I

FIG. 17.

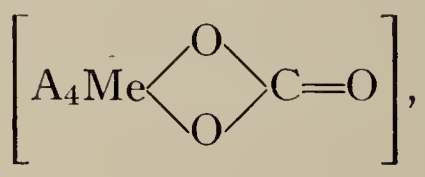


II

FIG. 18.

A ring formation involving two separated valencies is, on the face of the matter, highly improbable; the fact that the oxalato and carbonato salts, although they belong to the type MeA_4B_2, do not form stereoisomeric series shows that no such formation takes place. Formula II, which is the stereoisomer corresponding to Formula I, can not exist because of steric hindrance.

This conclusion holds in the case of carbonato salts. Here, also, in accordance with the formula



is an example of ring formation which is impossible between two spacially separated coordination positions.

The cis-form may therefore be assigned with certainty to the oxalato and carbonato salts.

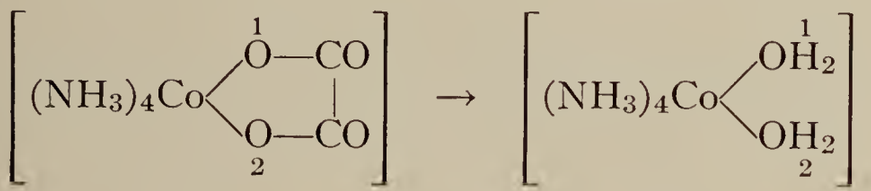
Another important proof of the correctness of this assumption lies in the fact that carbonato- and oxalato-dien-cobalti salts exhibit isomerism characterized by enantiomorphism, a phenomenon which, as will be shown later, can exist only in the case of cis-forms.[1]

Oxalato and carbonato salts, being indubitable cis-compounds, form the basis of configuration determinations. All

[1] See p. 70.

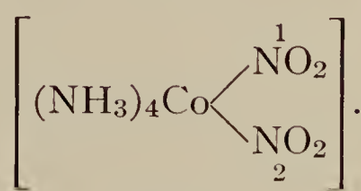
compounds of the type MeA_4B_2 which stand in generic relation to them, whether they can be obtained from them by direct decomposition or can be converted directly into them, must be considered cis-forms.

The isomerism of the previously mentioned flavo- and croceo-salts is explained by means of the following reactions: If oxalato- (or carbonato-) tetrammine-cobalti chloride (I) is treated with dilute hydrochloric acid, it is transformed [1] into the diaquo-tetrammine salt (II), which, therefore, is also a cis-form.



I

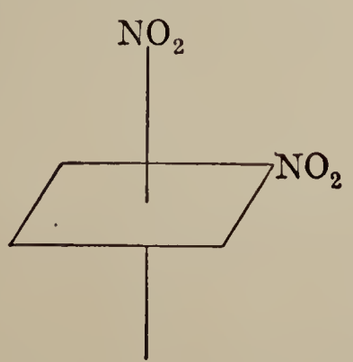
II



Flavo salt

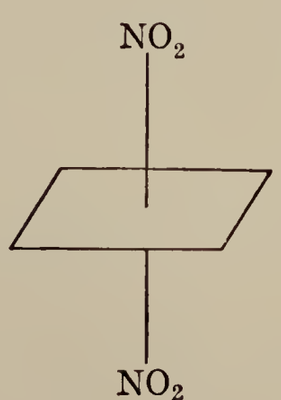
III

The brown flavo-salt (III) is formed by treating salt (II) with nitrous acid,[2] and it is therefore recognized as the 1,2-dinitro- or cis-compound. The isomeric croceo-salt is, accordingly, the trans- (1, 6) compound.



Flavo-series

FIG. 19.



Croceo-series

FIG. 20.

[1] S. M. Jörgensen, Z. anorg. Chem., **2**, 294 (1892).

[2] S. M. Jörgensen, Z. anorg. Chem., **5**, 162 (1894).

Salts of the croceo-series are never formed from 1,2-diaquo-salts, but result from the action of nitrous acid on nitro-pentammine salts,[1]

$$[Co(NH_3)_5NO_2](NO_2)_2+HNO_2$$

$$=N_2+2H_2O+\left[(NH_3)_4Co\begin{matrix}{}^{1}NO_2\\ {}_{6}NO_2\end{matrix}\right]NO_2,$$

or from 1,6-diaquo salts, which themselves are never formed from carbonato or oxalato salts.

Configuration of the Violeo- and Praseo-salts

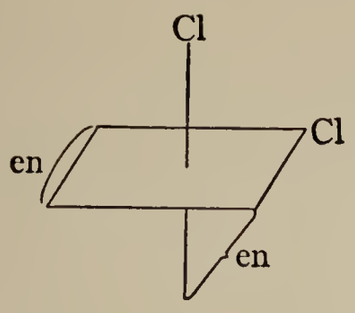
Dichloro- (dibromo-) dien-cobalti salts, belonging also to the type MeA_4B_2, are known in two isomeric series which are differentiated, according to their colors, as violeo- and praseo-salts.

The configuration of these salts is likewise derived from their relation to carbonato salts. If concentrated hydrochloric acid is allowed to act upon a carbonato-dien-cobalti salt, there results as a first reaction product the violeo-salt, although it is unstable in the presence of acids. Consequently it soon rearranges into the stable praseo-salt. It follows that the primary product of the reaction

$$\left[(en)_2Co\begin{matrix}{}^{1}O\\ {}_{2}O\end{matrix}CO\right]+2HCl=\left[(en)_2Co\begin{matrix}{}^{1}Cl\\ {}_{2}Cl\end{matrix}\right]+H_2O+CO_2$$

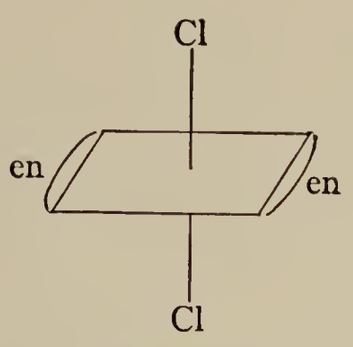
is the cis-compound. The praseo-salts therefore exist as trans-forms.

[1] S. M. Jörgensen, Z. anorg. Chem. **5**, 169 (1894); **17**, 472 (1898).



Violeo-series

FIG. 21.



Praseo-series

FIG. 22.

This proof of constitution is supported by the fact that violeo-salts are formed also by cautious heating of sulphito-dien-cobalti chloride with concentrated hydrochloric acid. Since this salt is a compound containing a closed ring (Fig. 23), it must belong to the cis-series.

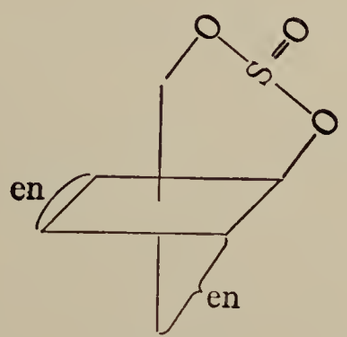


FIG. 23.

The determination of configuration of the previously mentioned chromium compounds of corresponding composition follows from their generic relation to oxalato-dien-chromi salts, which belong to the cis-series:

$$\left[(en)_2Cr\begin{matrix}O-CO\\ |\\ O-CO\end{matrix}\right]X.$$

From these are formed only violet dichloro- and dibromo-salts which are, therefore, cis-compounds. The green stereoisomeric trans-compounds are formed from one of the two isomeric dithiocyanato-dien-chromi salts—the yellowish-orange 1, 6- salt (Fig. 24)—through the replacement of the thiocyanate radicals by chlorine or bromine.

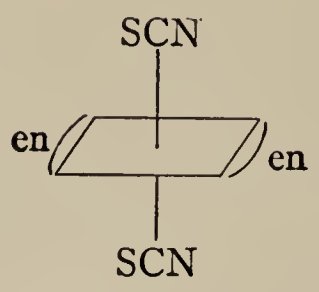
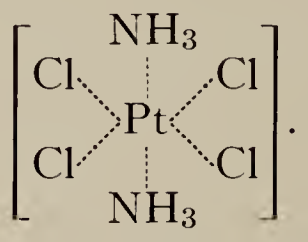
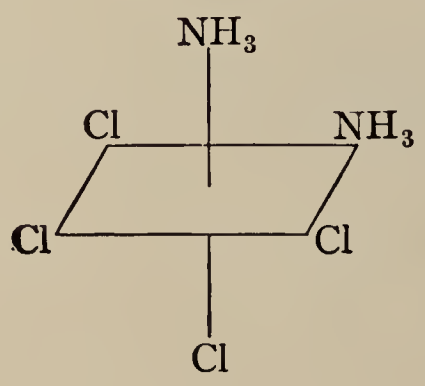


FIG. 24.

Finally, to this class belong the two isomers [1] of tetrachloro-diammine-platinum, $Pt(NH_3)_2Cl_4$, which has been mentioned previously. This compound was used in the second chapter to explain the principles of the coordination formulæ. On the basis of chemical properties both isomers possess the formula

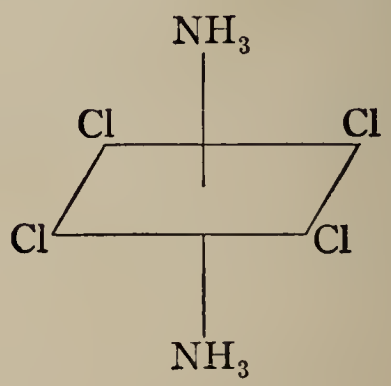


No structural difference of any kind is possible, and we must, therefore, be dealing with a case of stereoisomerism, a fact which is not remarkable, since the compound belongs to the type MeA_4B_2. The difference between these isomers and the cobalt and chromium salts already discussed lies only in the fact that in this case two ammonia molecules and four chlorine atoms are in the complex, as compared with four ammonia molecules and two chlorine atoms in the cobalt and chromium compounds. According to the previous discussion, the isomerism finds expression in the following formulæ.



Cis (orange)

FIG. 25.



Trans (yellow)

FIG. 26.

[1] A. Werner, "Lehrbuch der Stereochemie," p. 349; Fischer (Jena). 1904.

A direct determination of configuration in this case has not been possible up to the present time. However, from the structure of the two isomeric dichloro-diammine-platinum salts which, on addition of chlorine, form the isomers in question, it is concluded that the orange-colored compound is cis-tetrachloro-diammine-platinum, and the yellow, the trans-form. We shall return to the details of this relationship after a discussion of the compounds containing bivalent platinum.

b. Compounds of the Type MeA_2B_2

This type is represented chiefly by compounds of bivalent platinum, palladium, and copper. As examples we may mention:

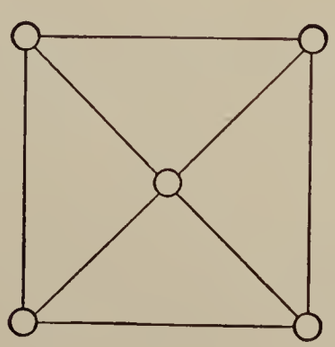
$[Pt(NH_3)_2Cl_2]$	$[Pd(Py)_2Cl_2]$	$[Cu(NH_3)_2(SCN)_2]$.
Dichloro-diammine-platinum	Dichloro-dipyridine-palladium	Dithiocyanato-diammine-copper

Special interest attaches to the existence of two isomeric forms of the platinum compound.[1] Since constitutional isomerism is precluded on the basis of chemical properties, here again spacial isomerism comes into consideration.

The spacial arrangement of a compound of the type MeA_2B_2 can be represented in two ways. Either the central atom, in analogy with the stereochemistry of carbon, may be placed in the center of a tetrahedron (I), or the four coordination positions may be placed in a plane configuration as corners of a quadrilateral, according to (II).

I

FIG. 27.

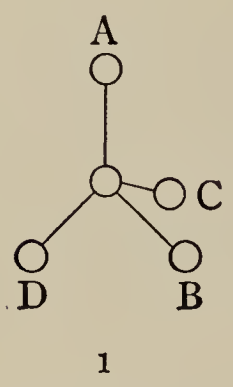


II

FIG. 28.

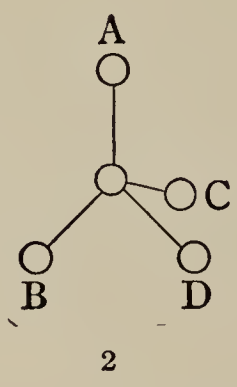
[1] A. Werner, "Lehrbuch der Stereochemie," p. 338.

However, the stereochemistry of carbon compounds shows that in the tetrahedral arrangement isomerism becomes possible only when all four substituents are different, or, for our purpose, in the case of the type Me(ABCD). Then there are formed two isomers, (1) and (2), which are in the relation of object and mirror-image.



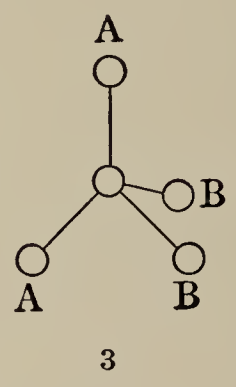
1

Fig. 29.



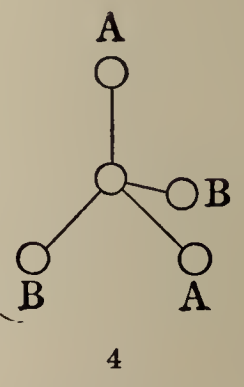
2

Fig. 30.



3

Fig. 31.

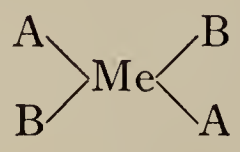


4

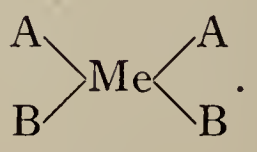
Fig. 32

In the type MeA_2B_2 under consideration, however, the two tetrahedra, (3) and (4), are identical. By a clockwise rotation of (4) through 120° this fact becomes apparent.

The structures drawn on the basis of Formula II can not be superimposed:



Trans



Cis

In this case there must be an isomeric pair of substances with cis- and trans-configurations.

The existence of two isomeric dichloro-diammine-platinum compounds proves that our conception of a spacially different arrangement in accordance with Formula II is correct.

The two isomers differ, as usual, in color: one, orange-yellow, is called plato-semidiammine chloride; the other, sulphur-yellow, is platosammine chloride.

Determination of Configuration MeA_2B_2 [1]

Without giving the reasons for our decision at this point, we assign to plato-semidiammine chloride Formula I (cis) and to platosammine chloride Formula II (trans):

The correctness of this assumption is proved by the following differences in chemical properties: If two molecules of pyridine are allowed to act upon plato-semidiammine chloride, the compound dipyridine-diammine-plato chloride is formed by a penetration reaction: [2]

$$\left[Pt\begin{matrix}(Py)_2\\(NH_3)_2\end{matrix}\right]Cl_2. \qquad (\alpha)$$

If two molecules of pyridine are added to platosammine chloride, a dipyridine-diammine-plato chloride is formed which is not identical with (α):

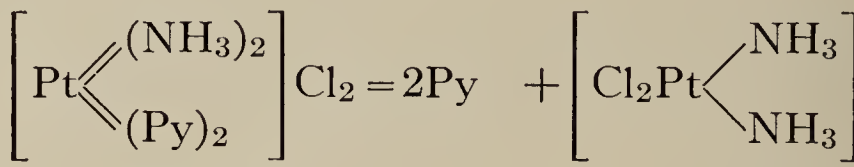
$$\left[Pt\begin{matrix}(Py)_2\\(NH_3)_2\end{matrix}\right]Cl_2. \qquad (\beta)$$

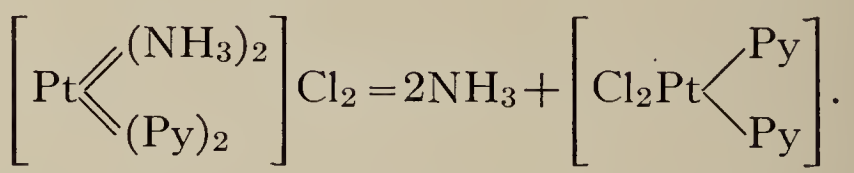
The two isomers show the following difference on heating: [3] (α) splits off one molecule of ammonia and one of pyridine, thus forming dichloro-pyridine-ammine-platinum:

$$\left[Pt\begin{matrix}(NH_3)_2\\(Py)_2\end{matrix}\right]Cl_2 = \left[Cl_2Pt\begin{matrix}NH_3\\Py\end{matrix}\right] + Py + NH_3.$$

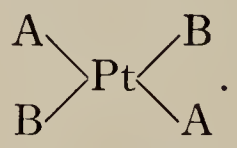
[1] A. Werner, " Lehrbuch der Stereochemie," pp. 338 ff.
[2] S. M. Jörgensen, J. prakt. Chem., [2] **33**, 510 (1886).
[3] A. Werner, Z. anorg. Chem., **3**, 310 (1893).

(β), on the other hand, loses either two molecules of ammonia or two of pyridine and forms a mixture of platosammine chloride and platopyridine chloride:



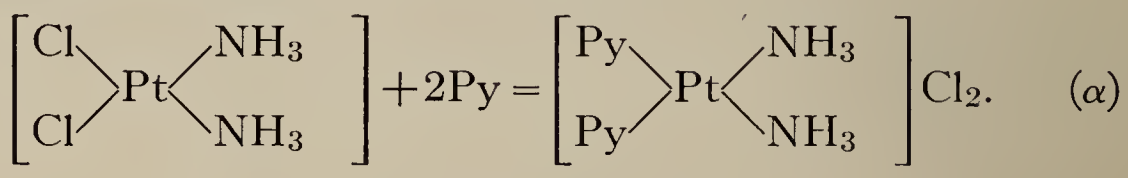


Both (α) and (β), therefore, are transformed by heating into compounds of the platosammine series, to which we have assigned the general formula

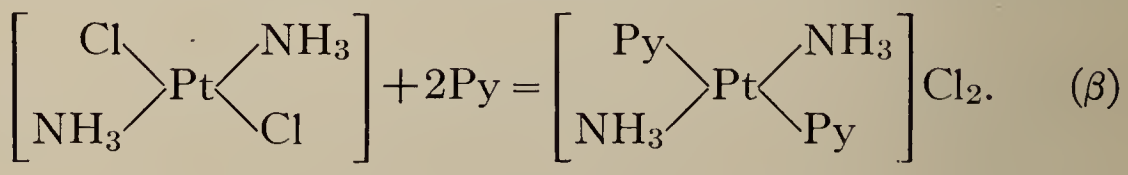


A question now arises: Does this behavior agree with the formulæ which we have already assigned to the two compounds?

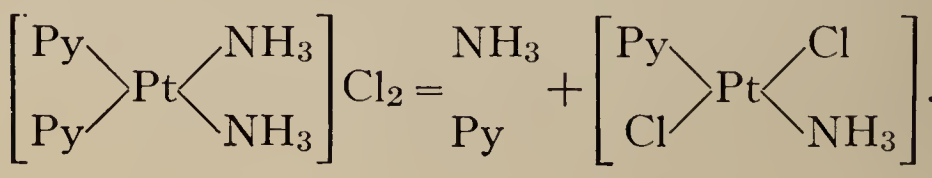
The semidiammine chloride should give:



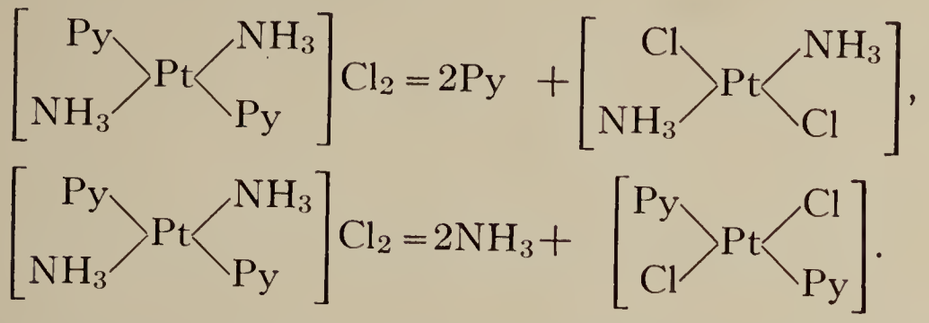
The ammine chloride should behave according to the equation:



If we consider (α), it is apparent that the transformation into the platosammine (trans) series can take place only by splitting off one ammonia and one pyridine molecule; from (α) a mixed compound, $PtNH_3PyCl_2$, of the following composition must result:



On the other hand, it is seen from (β) that a transformation into a trans-compound can take place in either of two ways—through loss of 2 NH_3 or of 2 Py:



The reactions which in reality take place are in complete agreement with those which we should expect from our formulation, and they therefore confirm the correctness of the respective formulæ.[1]

c. *Compounds of the Type* MeA_3B_3

On page 50 it was indicated that in the type MeA_3B_3, on the basis of the space formulæ, two isomers are to be expected. The difference is shown by the following figures.

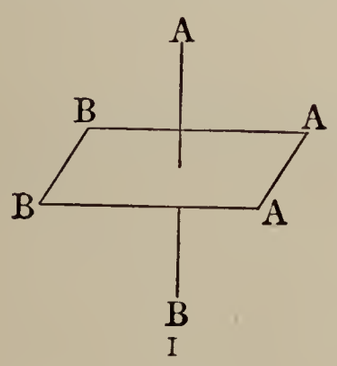


Fig. 33.

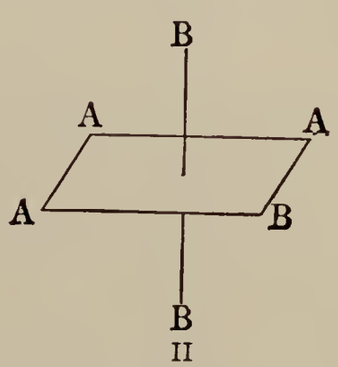


Fig. 34.

In Formula I the three A's lie at the corners of one face of an octahedron, whereas in Formula II they do not.

Examples of this type are, at the present time, very rare. Trinitro-trihydroxo-cobaltiate,[2]

$$[Co(NO_2)_3(OH)_3]Me_3,$$

[1] A. Werner, Z. anorg. Chem., **3**, 310 (1893).

[2] A. Rosenheim and A. Garfunkel, Ber., **44**, 1865 (1911).

is known in two isomeric forms, one vermilion and the other brownish-red. A method of determining the configuration is not yet known for this type. Nevertheless, the existence of two isomers is a still further proof of the correctness of the octahedral formula.

6. The Isomerism of Enantiomorphous Forms

If, in a complex compound of the type MeA_4B_2, the four A's are replaced by two bivalent groups, such as ethylene diamine, on the basis of the octahedral formula a still different type of spacial isomerism must become possible. Two forms of the cis-modification of such a compound may be pictured; these forms do not, indeed, differ in regard to the location of the individual components with respect to the central atom, but still are not identical, since they exist in the relation to each other of object and mirror-image.

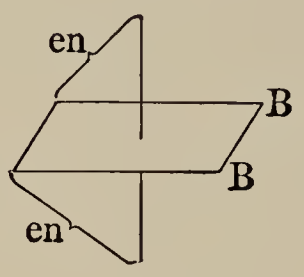


Fig. 35.

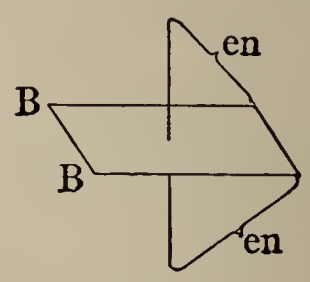


Fig. 36.

This kind of isomerism, many instances of which have been known for a long time in the field of organic chemistry, is therefore characterized by the existence of enantiomorphous forms.

As a matter of fact, it is also found possible, in the case of compounds of the type described, to prepare two enantiomorphs of the cis-form.[1] This is a striking proof of the correctness of the octahedral formula, a proof which is still more convincing because the trans-form has never been observed to exhibit

[1] A. Werner and V. L. King, Ber., **44**, 1887 (1911).

isomerism of this type and, on account of its symmetrical structure,

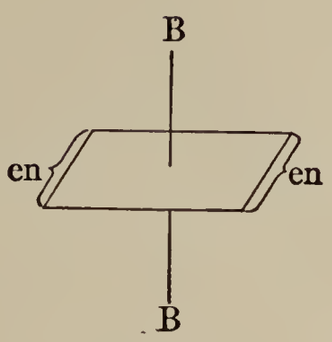


FIG. 37.

is not able to do so.

The asymmetry of the two isomeric cis-forms with identical structure requires that there should be no differences in chemical properties. Only two important differences of a physical nature are noticeable; first, the isomers form enantiomorphous crystals, i.e., crystals which are in the relation of object and mirror-image; second, either in the solid state or in solution, they rotate the plane of polarized light in opposite directions. For this reason they are said to be optically active; the lævo-rotating molecule is called the lævo-form (*l*) and the dextro-rotating, the dextro-form (*d*).

In the preparation of such an optically active complex compound, an equimolecular mixture of the antipodes is usually formed, in which *d*- and *l*-rotation are exerted simultaneously, so that the mixture at first appears to be optically inactive. The separation of this racemic mixture into the optically active components is completely analogous to the method used for carbon compounds [1] and is brought about by salt formation with an optically active base or acid, as the case may be.[2] The separation depends upon the fact that the two resulting compounds

$$A^d + B^d = (A^d B^d)$$

$$A^l + B^d = (A^l B^d)$$

[1] A. W. Stewart, "Stereochemistry," Chapter III.
[2] A. Werner and V. L. King, loc. cit.

possess different solubilities and may therefore be separated by fractional crystallization. The bases generally used for this purpose are quinine, strychnine and cinchonine; the acids are tartaric, camphorsulphonic, and bromcamphorsulphonic acids.

If, for example, the chloride of the racemic mixture is being used, a solution is treated with silver *d*-bromcamphorsulphonate, and thus the products obtained are insoluble silver chloride and the *d*-sulphonates of the *d*-form and of the *l*-form. The two salts may be separated from this solution by fractional crystallization.

Among the various members of the type $MeA_2^{II}B_2$, the following are known: dichloro-, dinitro-, and diammine-dien salts of cobalt:

$$\underset{\text{Violeo-series}}{[Co(en)_2Cl_2]X} \qquad \underset{\text{Flavo-series}}{[Co(en)_2(NO_2)_2]X} \qquad [Co(en)_2(NH_3)_2]X_3.$$

They exhibit cis-trans-isomerism, as stated previously, in the form of violeo- and praseo-, or flavo- and croceo-salts. The cis-forms, i.e., the violeo- and flavo-salts, are further separable into enantiomorphs. Also, the chromium compounds of the type of cis-dichloro-dien salts, $[Cr(en)_2Cl_2]X$, give isomers of the same kind.

The carbonato- and oxalato-dien salts of cobalt and chromium should receive special consideration. They do not show cis-trans-isomerism, but do show enantiomorphism. Hence, in these salts the acid radicals can not occupy the 1, 6-positions, since, as stated above, no mirror-images are formed in the trans-series; the acid radicals must occupy two adjacent positions as shown in the following figures.

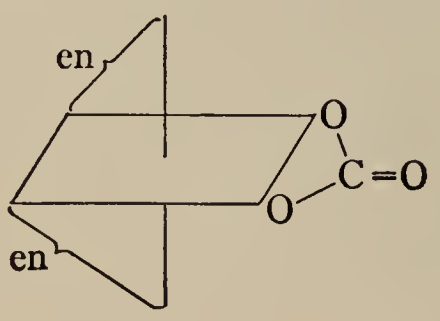


FIG. 38.

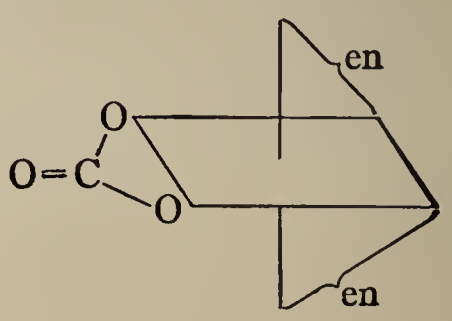


FIG. 39.

This proof of the assumption that carbonato and oxalato salts are cis-compounds plays, as we have already stated in a previous section, a very important part in the determination of configuration of the cis-trans-isomers.

Finally, it must be concluded that enantiomorphous forms also exist for compounds of the type $[Me(en)_3]$, according to the following diagrams.

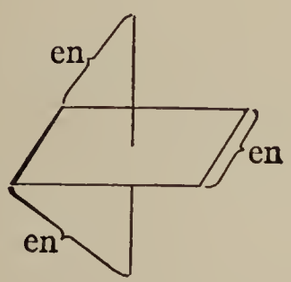


FIG. 40.

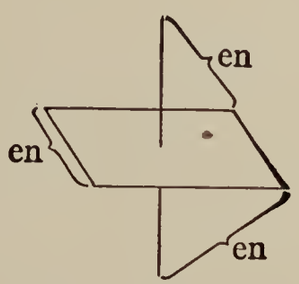
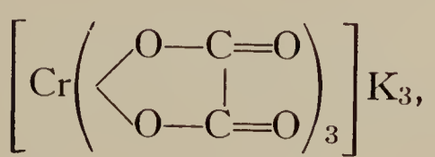


FIG. 41.

This case also has been realized experimentally. In cobalt, as well as in chromium and rhodium compounds, substances of this type have been prepared and separated into the optically active components. The separation was accomplished in the compound $[Co(en)_3]Cl_3$, for example, by the use of silver *d*-tartrate.[1]

Finally, in connection with the compounds of this type we must consider potassium trioxalato-chromiate,



$$\left[Cr\left(\begin{array}{l}O-C=O\\ \quad\ |\\ O-C=O\end{array}\right)_3\right]K_3,$$

in which the complex functions as an anion. This salt also exists, as is to be expected, in two enantiomorphous forms. In this case a base, strychnine, is used in the separation.[2] There are formed the strychnine salts of the *l*- and *d*-forms of trioxalato-chromi acid and the antipodes are separated by fractional crystallization from alcoholic solution.

[1] A. Werner, Ber., **45**, 121 (1912).
[2] A. Werner, Ber., **45**, 3061 (1912)

The fact that all the cases which must be assumed to exist on the basis of this primary, purely hypothetical octahedral formula can be actually realized, must be regarded as a conclusive proof of our formulation of the structure of the complex compounds.

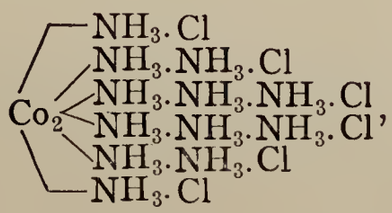
CHAPTER IV

HISTORICAL REVIEW

In connection with the study of the Coordination Theory, it may not be uninteresting to learn something of a few earlier views in regard to the constitution of compounds of the higher order.

As early as the first half of the previous century, these compounds, which could not be brought into accord with the precursors of the valence theory, attracted the interest of the chemist to a great extent. After many inadequate theories had been proposed and soon abandoned, C. W. Blomstrand [1] was the first to succeed, in some degree, in explaining the constitution of the metal ammines.[2]

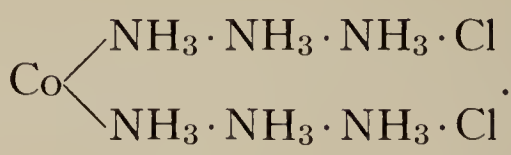
In analogy with the chain formulæ of organic chemistry he assumed for these compounds similar chain formulæ with ammonia molecules linked to each other. The formation of the chain was explained by the assumption of quinquivalent nitrogen. The fact that the number six plays an important part in the addition of ammonia molecules to metal salts had already been pointed out by Blomstrand. From the prevailing belief at that time that cobalt chloride possessed the bimolecular formula Co_2Cl_6, he gave the following formula to hexammine-cobalti chloride:



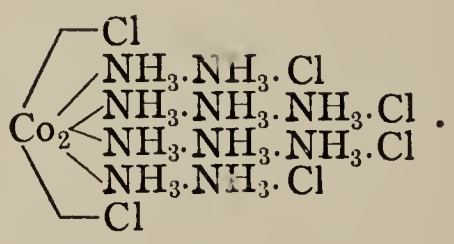
[1] " Die Chemie der Jetztzeit," p. 280, Heidelberg (1869); J. prakt. Chem., [2] **3**, 206 (1871).

[2] A similar explanation of the constitution of hydrates was proposed independently by A. Würtz, " La Théorie Atomique," Paris (1879).

and to hexammine-cobalto chloride the formula:

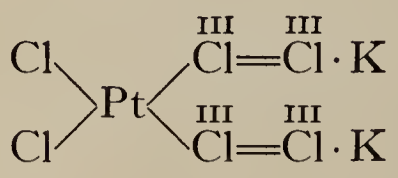


Blomstrand assumed the unsymmetrical distribution of the ammonia molecules in hexammine-cobalti chloride to be able to give the pentammine chloride the analogous formula



In this compound two chlorine atoms possess properties different from those of the other four, an experimental fact with which he was already acquainted. By the loss of ammonia, two chlorine atoms have entered into direct union with the cobalt atom and, therefore, are no longer as active. In this example we see the first advance toward the conception of direct and ionizable linkages later put forward by Werner.

For the double halides, Blomstrand, in a similar manner, assumed a catenation of the halogen atoms with a partial increase in their valence and gave, for example, the formula



to K_2PtCl_6. As can be seen from our previous discussion, such a formula is in contradiction to the wholly identical character of all the chlorine atoms.

A far-reaching advance in the chemistry of the complex compounds, especially in regard to numerous experimental researches, is due to Jörgensen.[1] From molecular weight determinations

[1] Many papers in J. prakt. Chem. and Z. anorg. Chem., 1877–1899.

he demonstrated that the metal ammines possess the simple molecular formulæ, and accordingly expressed the structure of the hexammine chloride as

$$\left.\begin{matrix} Cl\cdot H_3N \\ Cl\cdot H_3N \end{matrix}\right\rangle Co\cdot NH_3\cdot NH_3\cdot NH_3\cdot NH_3\cdot Cl,$$

and of the pentammine as

$$\left.\begin{matrix} Cl \\ Cl\cdot NH_3 \end{matrix}\right\rangle Co\cdot NH_3\cdot NH_3\cdot NH_3\cdot NH_3\cdot Cl.$$

All these formulæ, however, are incorrect, since according to them no valencies remain for the ammonia molecules in the triacido-compounds, for example $[Co(NH_3)_3(NO_2)_3]$, if all three acid radicals are attached to the central atom, which must of necessity be the case in such compounds from their very low electrical conductivities.[1] To this compound, however, Jörgensen gave the formula

$$Co\begin{matrix} NO_2 \\ -NH_3\cdot NH_3\cdot NH_3\cdot NO_2, \\ NO_2 \end{matrix}$$

thus assuming an indirect linkage for one nitrite radical. From the proof brought forward by Werner to the effect that the compound is a non-electrolyte, this type of formula fell into disrepute and was finally replaced by Werner's ideas.[2]

[1] See p. 20.

[2] Other theories which have been advanced with regard to the structure of complex compounds may be found in the following references: L. Spiegel, Z. anorg. Chem., **29**, 365 (1902). S. Arrhenius, "Theorien der Chemie," p. 73 (1906). S. H. C. Briggs, J. Chem. Soc., **93**, 1564 (1908). W. Ramsay, ibid., **93**, 774 (1908). J. A. N. Friend, ibid., **93**, 260, 1006 (1908); **109**, 715 (1916); "The Theory of Valency," p. 150; Longmans (London) (1909). J. M. Nelson and K. G. Falk, J. Am. Chem. Soc., **37**, 274 (1915). H. S. Fry, "The Electronic Conception of Valence and the Constitution of Benzene," pp. 257–271; Longmans (London) 1921.

As we have seen, the Coordination Theory explains the origin and the chemical and physical properties of compounds of the higher order without exceptions or contradictions. The most important support of this almost purely hypothetical formulation of the structure of complex compounds is the fact that, up to the present time, all the phenomena predicted by this hypothesis, in particular the existence of certain isomeric compounds, have been realized by experiment.

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